

# ARKIV FÖR MINERALOGI OCH GEOLOGI

UTGIVET AV

K. SVENSKA VETENSKAPS-  
AKADEMIEN

---

Band 2 . Häfte 4

---



ALMQVIST & WIKSELL / STOCKHOLM

1958



# The crystal structure of mendipite, $\text{Pb}_3\text{O}_2\text{Cl}_2$

By O. GABRIELSON

With 1 figure in the text

## Previous investigations

Mendipite was first analysed by J. Berzelius (1823) on material from Mendip Hills, England. He found the composition of the mineral to be  $\text{PbCl}_2 \cdot 2\text{PbO}$ . Somewhat later (1825) a crystallographic description was performed by W. Haidinger, who described the mineral as orthorhombic.

Mendipite has also been found at Brilon, Germany, and at Långban, Sweden. Mendipite from Långban was discovered as early as about 1930, and a description was intended to be published by G. Aminoff, but was never completed. J. Goñi and C. Guillemin has later (1953) made a short description of mendipite from Långban.

An X-ray investigation by F. A. Bannister (1934) gave the following unit cell dimensions of mendipite:  $a=9.50 \text{ \AA}$ ,  $b=11.87 \text{ \AA}$ , and  $c=5.87 \text{ \AA}$ . According to Bannister the unit cell contains four molecules  $\text{Pb}_3\text{O}_2\text{Cl}_2$ .

*Material.*—Two prismatic crystals, elongated parallel to their  $c$ -axes, were selected from a collection of mendipite crystals from Långban. The crystals were used for X-ray photographs parallel and perpendicular to the  $c$ -axes.

*Unit cell and space group.*—Equi-inclination photographs were taken around the  $c$ -axes using unfiltered copper radiation. The unit cell dimensions found are  $a=9.52 \text{ \AA}$ ,  $b=11.95 \text{ \AA}$ , and  $c=5.87 \text{ \AA}$ , which are, within the limits of error, equal to those found by F. A. Bannister.

The Weissenberg photographs obtained registered the reflections  $kh0$ ,  $hk1$  and  $hk2$ . By studying the systematic extinctions, it was found that reflections  $h00$  and  $0k0$  are present only for  $h$  and  $k=2n$ . These conditions are satisfied only in the space groups  $P 2_12_12$  and  $P 2_12_12_1$ .

Table 1. The finally accepted parameters.

4 $\text{Pb}_I$	in $x=0.119$ , $y=0.219$ , $z=0.250$
4 $\text{Pb}_{II}$	in $x=0.335$ , $y=0.082$ , $z=0.750$
4 $\text{Pb}_{III}$	in $x=0.453$ , $y=0.437$ , $z=0.250$
4 $\text{O}_I$	in $x=0.645$ , $y=0.430$ , $z=0.000$
4 $\text{O}_{II}$	in $x=0.645$ , $y=0.430$ , $z=0.500$
4 $\text{Cl}_I$	in $x=0.370$ , $y=0.520$ , $z=0.750$
4 $\text{Cl}_{II}$	in $x=0.465$ , $y=0.195$ , $z=0.250$



Table 2. Weissenberg photograph of Mendipite. Rotation axis [001]. Zero layer line. Cu-radiation. Comparison between observed and calculated structure factors, using only the positions of the lead atoms for the calculation of the structure factors.

$hkl$	$ F $ obs	$ F $ calc	$hkl$	$ F $ obs	$ F $ calc	$hkl$	$ F $ obs	$ F $ calc	$hkl$	$ F $ obs	$ F $ calc
0 1 0	< 5	0	2 1 0 0	15	15	5 8 0	31	24	8 4 0	22	17
0 2 0	< 5	9	2 1 1 0	27	30	5 9 0	< 15	8	8 5 0	31	25
0 3 0	< 5	0	2 1 2 0	15	9	5 10 0	< 15	8	8 6 0	< 15	10
0 4 0	< 10	6	2 1 3 0	13	12	5 11 0	< 15	2	8 7 0	< 15	4
0 5 0	< 10	0				5 12 0	< 10	10	8 8 0	22	17
0 6 0	26	54	3 0 0	< 5	0	5 13 0	26	26	8 9 0	20	21
0 7 0	< 10	0	3 1 0	8	15				8 10 0	11	11
0 8 0	23	35	3 2 0	14	29	6 0 0	18	13	8 11 0	14	17
0 9 0	< 15	0	3 3 0	22	20	6 1 0	35	30			
0 10 0	< 15	2	3 4 0	39	51	6 2 0	21	13	9 0 0	< 15	0
0 11 0	< 15	0	3 5 0	19	23	6 3 0	< 10	4	9 1 0	< 15	5
0 12 0	< 15	6	3 6 0	< 10	2	6 4 0	18	14	9 2 0	< 15	10
0 13 0	< 15	0	3 7 0	< 10	5	6 5 0	34	30	9 3 0	< 15	7
0 14 0	39	38	3 8 0	< 15	2	6 6 0	25	16	9 4 0	< 15	12
			3 9 0	26	30	6 7 0	< 15	4	9 5 0	< 15	8
1 0 0	< 5	0	3 10 0	34	38	6 8 0	< 15	7	9 6 0	< 15	5
1 1 0	9	19	4 0 0	17	30	6 9 0	15	10	9 7 0	< 10	1
1 2 0	6	16	4 1 0	< 10	5	6 10 0	< 10	8	9 8 0	37	29
1 3 0	7	14	4 2 0	17	24	6 11 0	< 10	6	9 9 0	13	14
1 4 0	< 10	2	4 3 0	< 10	4	6 12 0	23	19	9 10 0	< 5	9
1 5 0	< 10	1	4 4 0	< 10	11	6 13 0	26	28	9 11 0	< 5	2
1 6 0	19	33	4 5 0	< 10	7	7 0 0	< 15	0	10 0 0	35	21
1 7 0	23	28	4 6 0	17	15	7 1 0	< 15	6	10 1 0	35	22
1 8 0	< 10	8	4 7 0	20	16	7 2 0	< 15	13	10 2 0	34	24
1 9 0	15	19	4 8 0	< 15	2	7 3 0	< 15	4	10 3 0	< 15	2
1 10 0	< 15	9	4 9 0	< 15	9	7 4 0	32	27	10 4 0	< 10	10
1 11 0	< 15	4	4 10 0	15	16	7 5 0	27	21	10 5 0	12	14
1 12 0	25	26	4 11 0	< 15	8	7 6 0	< 15	2	10 6 0	19	20
1 13 0	21	19	4 12 0	< 10	3	7 7 0	15	18	10 7 0	12	10
1 14 0	13	13	4 13 0	16	18	7 8 0	> 15	0	10 8 0	25	21
			4 14 0	21	15	7 9 0	< 10	2	11 0 0	< 10	0
2 1 0	< 5	10	5 0 0	< 10	0	7 10 0	19	23	11 1 0	< 10	9
2 2 0	< 5	5	5 1 0	34	45	7 11 0	35	29	11 2 0	23	20
2 3 0	31	63	5 2 0	15	16	7 12 0	< 10	3	11 3 0	< 10	8
2 4 0	< 10	6	5 3 0	8	2	7 13 0	< 5	2	11 4 0	30	18
2 5 0	< 10	11	5 4 0	< 10	6	8 0 0	10	4	11 5 0	23	24
2 6 0	< 10	4	5 5 0	14	11	8 1 0	28	20	11 6 0	19	17
2 7 0	< 10	0	5 6 0	14	16	8 2 0	37	32			
2 8 0	< 10	12	5 7 0	46	48	8 3 0	37	26			
2 9 0	19	19									

A Weissenberg photograph of a crystal oriented perpendicular to the  $c$ -axis showed that reflections  $00l$  only are present for  $l=2n$ . Under such conditions only the space group  $P2_12_12_1$  (No. 19), is possible.

*Atomic positions.*—The atomic positions and symmetry elements of the space group  $P2_12_12_1$  are (according to I.T. 1952):

4: (a)  $x y z$ ;  $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$ ;  $\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$ ;  $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$ .

Point symmetry: 1 in (a).

Table 3. Weissenberg photograph of Mendipite. Rotation axis [001]. First layer line. Cu-radiation. Comparison between observed and calculated structure factors, using only the positions of the lead atoms for the calculation of the structure factors.

$hkl$	$ F $ obs	$ F $ calc	$hkl$	$ F $ obs	$ F $ calc	$hkl$	$ F $ obs	$ F $ calc	$hkl$	$ F $ obs	$ F $ calc
0 1 1	<10	0	2 10 1	<10	4	5 0 1	9	12	7 11 1	16	14
0 2 1	10	35	2 11 1	<10	6	5 1 1	12	7	8 0 1	<15	0
0 3 1	<10	0	2 12 1	11	13	5 2 1	20	15	8 1 1	27	27
0 4 1	30	69	2 13 1	26	28	5 3 1	42	55	8 2 1	25	25
0 5 1	<10	0	2 14 1	14	16	5 4 1	23	19	8 3 1	17	9
0 6 1	<10	4				5 5 1	21	24	8 4 1	20	8
0 7 1	<10	0	3 0 1	32	63	5 6 1	<15	1	8 5 1	24	24
0 8 1	<10	3	3 1 1	16	30	5 7 1	<15	2	8 6 1	29	25
0 9 1	<15	0	3 2 1	<10	11	5 8 1	<15	3	8 7 1	28	21
0 10 1	34	51	3 3 1	<10	2	5 9 1	25	23	8 8 1	32	23
1 0 1	<10	9	3 4 1	<10	1	5 10 1	<15	1	8 9 1	23	17
1 1 1	<5	11	3 5 1	22	29	5 11 1	30	31			
1 2 1	14	32	3 6 1	26	40	5 12 1	23	18	9 0 1	17	15
1 3 1	17	33	3 7 1	<10	1	6 0 1	<10	0	9 1 1	15	4
1 4 1	<10	8	3 8 1	21	26	6 1 1	18	15	9 2 1	17	14
1 5 1	<10	5	3 9 1	<15	9	6 2 1	20	18	9 3 1	<15	0
1 6 1	<10	3	3 10 1	<15	5	6 3 1	28	20	9 4 1	28	20
1 7 1	10	8	3 11 1	<15	5	6 4 1	15	12	9 5 1	16	11
1 8 1	15	15	3 12 1	<15	11	6 5 1	28	24	9 6 1	<10	0
1 9 1	11	13	3 13 1	23	23	6 6 1	<15	2	9 7 1	<10	2
1 10 1	17	23	3 14 1	27	27	6 7 1	<15	2	9 8 1	10	24
1 11 1	<15	11				6 8 1	25	20	10 0 1	<15	0
1 12 1	<15	1	4 0 1	<10	0	6 9 1	40	34	10 1 1	11	27
1 13 1	15	20	4 1 1	<10	4	6 10 1	17	10	10 2 1	26	24
1 14 1	12	12	4 2 1	<10	5				10 3 1	10	3
			4 3 1	<10	6	7 0 1	27	33	10 4 1	25	22
2 0 1	<5	0	4 4 1	20	19	7 1 1	20	20	10 5 1	31	10
2 1 1	15	43	4 5 1	<10	11	7 2 1	<15	3	10 6 1	27	18
2 2 1	<5	4	4 6 1	21	26	7 3 1	16	15			
2 3 1	<10	9	4 7 1	<15	6	7 4 1	<15	2			
2 4 1	10	35	4 8 1	12	12	7 5 1	<15	3			
2 5 1	<10	3	4 9 1	12	13	7 6 1	18	21			
2 6 1	<10	12	4 10 1	25	21	7 7 1	25	17			
2 7 1	29	52	4 11 1	29	21	7 8 1	16	14			
2 8 1	11	10	4 12 1	19	18	7 9 1	17	11			
2 9 1	<10	8	4 13 1	9	5	7 10 1	<10	2			

As the cell contains four molecules  $Pb_3O_2Cl_2$ , we have to locate twelve lead, eight oxygen and eight chlorine atoms. Lead is placed in three fourfold positions (a), oxygen and chlorine in two fourfold positions (a).

From the trial and error method, refined by means of the Fourier synthesis, the positions of the lead atoms were deduced. The positions of the oxygen and chlorine atoms have not been found in this way on account of their inconsiderable influence on the observed structure factors, and the observed structure factors have not been measured accurately enough for a successful location of these eight atoms. They have therefore been located on spatial considerations.

The finally accepted parameter values are shown in Table 1.



Table 4. Weissenberg photograph of Mendipite. Rotation axis [001]. Second layer line. Cu-radiation. Comparison between observed and calculated structure factors, using only the positions of the lead atoms for the calculated structure factors.

$hkl$	$ F $ obs	$ F $ calc	$hkl$	$ F $ obs	$ F $ calc	$hkl$	$ F $ obs	$ F $ calc	$hkl$	$ F $ obs	$ F $ calc
0 7 2	< 5	0	4 0 2	15	28	6 2 2	15	13	8 5 2	30	24
0 8 2	20	33	4 1 2	< 5	5	6 3 2	< 5	1	8 6 2	20	10
1 6 2	15	31	4 2 2	20	22	6 4 2	20	13	8 7 2	< 10	4
1 7 2	20	26	4 3 2	< 5	3	6 5 2	30	29	8 8 2	25	17
1 8 2	< 5	7	4 4 2	10	11	6 6 2	20	15	8 9 2	20	21
2 0 2	5	11	4 5 2	< 5	7	6 7 2	< 10	4			
2 1 2	< 5	9	4 6 2	15	14	6 8 2	< 10	7	9 0 2	< 10	0
2 2 2	< 5	7	4 7 2	25	15	6 9 2	< 10	9	9 1 2	10	5
2 3 2	25	57	4 8 2	< 10	2	6 10 2	< 10	8	9 2 2	10	10
2 4 2	< 5	7	4 9 2	15	9	6 11 2	< 10	6	9 3 2	< 10	7
2 5 2	< 5	10	4 10 2	20	16	6 12 2	20	19	9 4 2	15	11
2 6 2	< 5	3	4 11 2	< 10	8				9 5 2	< 10	8
2 7 2	< 5	0	5 0 2	< 5	0	7 0 2	< 5	0	9 6 2	10	5
2 8 2	< 5	12	5 1 2	25	42	7 1 2	< 10	5	9 7 2	< 10	1
2 9 2	15	18	5 2 2	10	15	7 2 2	< 10	13	9 8 2	35	28
2 10 2	< 10	14	5 3 2	< 5	2	7 3 2	< 10	4	9 9 2	15	14
2 11 2	15	29	5 4 2	< 5	6	7 4 2	25	26			
3 0 2	< 5	0	5 5 2	15	15	7 5 2	15	21	10 0 2	30	21
3 1 2	10	14	5 6 2	20	15	7 6 2	< 10	2	10 1 2	30	22
3 2 2	20	27	5 7 2	35	46	7 7 2	< 10	17	10 2 2	25	23
3 3 2	20	18	5 8 2	20	23	7 8 2	< 10	0	10 3 2	< 10	2
3 4 2	25	47	5 9 2	< 10	8	7 9 2	< 10	2	10 4 2	< 10	9
3 5 2	15	22	5 10 2	< 10	8	7 10 2	20	22	10 5 2	10	13
3 6 2	< 5	2	5 11 2	< 10	2	7 11 2	30	28	10 6 2	15	19
3 7 2	< 5	2	5 12 2	< 10	9	8 0 2	20	4	10 7 2	10	10
3 8 2	< 10	5	5 13 2	25	25	8 1 2	25	20	11 1 2	10	9
3 9 2	20	29	6 0 2	15	13	8 2 2	30	31	11 2 2	20	20
3 10 2	25	36	6 1 2	25	26	8 3 2	30	25	11 3 2	10	8
						8 4 2	20	17	11 4 2	25	18

A comparison between observed and calculated structure factors, obtained with the parameters of the lead atoms, is given in tables 2, 3 and 4. The influence of the anions on the structure factors have been neglected in the calculations.

*Description of the structure.*—In figure 1 the structure of mendipite is shown in projection on (001).

In the unit cell the lead atoms are arranged in two groups of each six atoms. The groups are oriented in a diagonal direction of the unit cell. The lead atoms of each group are placed in the corners of two tetrahedra, which are linked together along one edge. The oxygen atoms occupy the centres of these tetrahedra, which thus are held together by the Pb–O bonds. The bonds are rather short (2.33 Å) and therefore of covalent character. The theoretical covalent value of the Pb–O bond is according to Byström (1950):  $\text{Pb} (=1.56) + \text{O} (=0.74) = 2.30 \text{ Å}$ . The lead and oxygen atoms form  $\text{Pb}_6\text{O}_4$  tetrahedra, each of which shares one edge with one tetrahedron in the adjacent over- and underlying unit cell, thus forming infinite chains in the direction of the *c*-axes. The fibrous and columnar habit of the mendipite crystals obviously depends on these chains, which are longitudinally held together by the strong Pb–O bonds.

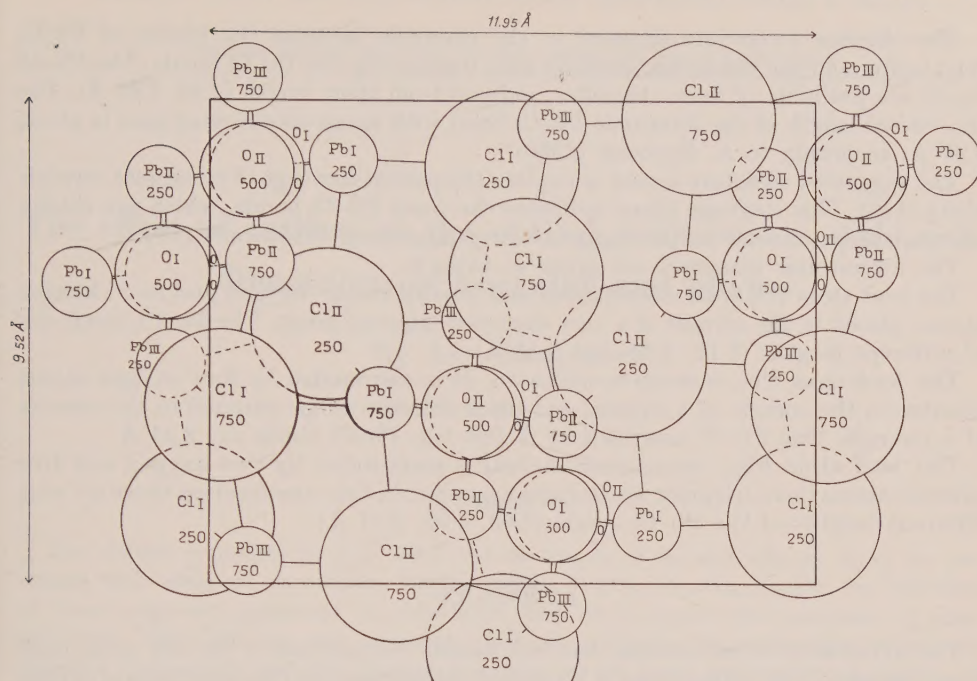


Fig. 1. The structure of mendipite, projected on (001). Superimposed oxygen atoms are symmetrically displaced.

Table 5. Interatomic distances in mendipite.

Atom	Coordi- nation	Number of atoms	Kinds of atoms	Distance (Å)
Pb <sub>I</sub>	6	2	O <sub>I</sub> , O <sub>II</sub>	2.33
		1	Cl <sub>I</sub>	3.12
		1	Cl <sub>II</sub>	3.25
		2	Cl <sub>II</sub>	3.44
Pb <sub>II</sub>	7	2	O <sub>I</sub>	2.33
		2	O <sub>II</sub>	2.33
		1	Cl <sub>I</sub>	2.95
		2	Cl <sub>II</sub>	3.44
Pb <sub>III</sub>	7	2	O <sub>I</sub> , O <sub>II</sub>	2.33
		2	Cl <sub>I</sub>	3.21
		1	Cl <sub>I</sub>	3.02
		2	Cl <sub>II</sub>	2.93
			O <sub>I</sub> —O <sub>II</sub>	2.62, 2.93
			Cl <sub>I</sub> —Cl <sub>I</sub>	3.70
			Cl <sub>I</sub> —Cl <sub>II</sub>	3.89
			Cl <sub>I</sub> —O <sub>I</sub> , O <sub>II</sub>	3.20
			Cl <sub>II</sub> —O <sub>I</sub> , O <sub>II</sub>	3.15–3.45



The chlorine atoms are situated in the channels between the chains of  $\text{Pb}_6\text{O}_4$  tetrahedra, and the chains are laterally held together by the Pb-Cl bonds. The Pb-Cl bonds are probably of ionic character, judging from their length (2.93–3.44 Å). The theoretical length of the interionic Pb-Cl bond with seven-coordinated lead is about 2.98 Å, according to A. Byström (1950).

The suggested structure seems to explain the perfect cleavage of mendipite crystals along (110). This cleavage plane indicates the weak Pb-Cl bonds, which are chiefly oriented perpendicular to the diagonal directions along (110) and ( $\bar{1}\bar{1}0$ ).

The interatomic distances are given in table 5.

The lead atom  $\text{Pb}_\text{I}$  is six-coordinated and bonded to two oxygen and four chlorine atoms, placed in the corners of a very distorted trigonal prism. The Pb-Cl bonds are of different lengths (3.12, 3.25 and 3.44 Å).

The lead atom  $\text{Pb}_\text{II}$  is seven-coordinated. It is surrounded by four oxygen atoms situated in the corners of a square, and three chlorine atoms situated in the corners of a triangle. One Pb-Cl bond is 2.95 Å and two Pb-Cl bonds are 3.44 Å.

The lead atom  $\text{Pb}_\text{III}$  (seven-coordinated) is surrounded by two oxygen and five chlorine atoms in an irregular spatial arrangement. In this coordination there are also different lengths of the Pb-Cl bonds (2.93, 3.02, 3.21 Å).

## SUMMARY

The crystal structure of mendipite has been studied. The positions of the lead atoms have been determined from the intensities of Weissenberg photographs, and the coordinates of oxygen and chlorine determined from space considerations.

Results: Space group  $P 2_12_12_1$  (No. 19).  $a = 9.52$  Å,  $b = 11.95$  Å,  $c = 5.87$  Å.

4 $\text{Pb}_\text{I}$	in $x = 0.119$ ,	$y = 0.219$ ,	$z = 0.250$
4 $\text{Pb}_\text{II}$	in $x = 0.335$ ,	$y = 0.082$	$z = 0.750$
4 $\text{Pb}_\text{III}$	in $x = 0.453$ ,	$y = 0.437$ ,	$z = 0.250$
4 $\text{O}_\text{I}$	in $x = 0.645$ ,	$y = 0.430$ ,	$z = 0.000$
4 $\text{O}_\text{II}$	in $x = 0.645$ ,	$y = 0.430$ ,	$z = 0.500$
4 $\text{Cl}_\text{I}$	in $x = 0.370$ ,	$y = 0.520$ ,	$z = 0.750$
4 $\text{Cl}_\text{II}$	in $x = 0.465$ ,	$y = 0.195$ ,	$z = 0.250$

$\text{Pb}_6\text{O}_4$  tetrahedra form infinite chains in the directions of the  $c$ -axis. These chains are laterally held together by the Pb-Cl bonds. Judging from the lengths of the bonds, the Pb-O bonds seem to be chiefly of covalent character and the Pb-Cl bonds of chiefly ionic character.

## REFERENCES

- BANNISTER, F. A., The crystal structure and optical properties of matlockite ( $\text{PbFCl}$ ). *Min. Mag.* 23, 587 (1934).  
 BYSTRÖM, A., Studies on Oxides and Fluorides of Lead. Stockholm, 1950.  
 GOŇI, J., and GUILLEMIN, C., La mendipite de Långban, Vermland, Suède. *Bull. Soc. Franç. Min. et Crist.* 76, 216 (1953).

Tryckt den 15 oktober 1957

Uppsala 1957. Almqvist & Wiksells Boktryckeri AB



# The effect of cations on the optical properties and the cell-dimensions of knebelite and olivine

By ÅKE HENRIQUES

With 1 figure in the text

## SUMMARY

The optical properties ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $2V_\alpha$ ) and the lengths of the unit cells ( $a_0$ ,  $b_0$ ,  $c_0$ ) are correlated with chemical composition for the system  $\text{Fe}_2\text{SiO}_4$ – $\text{Mn}_2\text{SiO}_4$ – $\text{Mg}_2\text{SiO}_4$  by derivation of linear regression equations in accordance with Hori's earlier determinations of clinopyroxenes. Equations are also presented which are valid when the relationship between the chemical composition and the physical properties are not linear but satisfies an equation of second degree. Comparisons between the two methods of calculation are made for the knebelite group of minerals.

## Introduction

Hori (1954) has correlated the optical properties of clinopyroxenes with their chemical composition. He used Hess's (1949) optical determinations as well as the corresponding analyses of about forty clinopyroxenes as the basis for this investigation. By deriving partial regression equations for refractive index and optic axial angle he has been able to establish the effect of the elements: ( $\text{Si}^{4+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) on the optical properties of the clinopyroxenes. His equations are:

$$\alpha = a_\alpha + \sum a_{i\alpha} N_i, \quad (1)$$

$$\beta = a_\beta + \sum a_{i\beta} N_i, \quad (2)$$

$$\gamma = a_\gamma + \sum a_{i\gamma} N_i, \quad (3)$$

$$2V = a_{2V} + \sum a_{i2V} N_i, \quad (4)$$

where  $a_\alpha$ ,  $a_\beta$ ,  $a_\gamma$ , and  $a_{2V}$  are constants,  $a_{i\alpha}$ ,  $a_{i\beta}$ ,  $a_{i\gamma}$ , and  $a_{i2V}$  represent the effects of the cation of type  $i$  on the refractive indices  $\alpha$ ,  $\beta$ ,  $\gamma$ , and the optic axial angle  $2V$ .  $N_i$  is the number of the cations in a fixed volume.

The partial regression equations possess solely descriptive character and rely entirely on the assumption that the optical properties are additively composed of and are linear functions of the relative contents of the elements. This should be the case, at least approximately, within a mineral group showing substitution

solid solution and whose properties vary continuously with the composition. Now, polarization effects and other lattice effects are able to influence the optical properties to some extent so that these deviate from the strictly linear function. As a result hereof full agreement between the determined and calculated values cannot be obtained. Better agreement between reckoned and observed values is obtained by using equations of the form:

$$\alpha = a_{\alpha} + \sum a_{i\alpha} N_i + \sum a'_{i\alpha} N_i^2, \quad (5)$$

$$\beta = a_{\beta} + \sum a_{i\beta} N_i + \sum a'_{i\beta} N_i^2, \quad (6)$$

$$\gamma = a_{\gamma} + \sum a_{i\gamma} N_i + \sum a'_{i\gamma} N_i^2, \quad (7)$$

$$2V = a_{2V} + \sum a_{i2V} N_i + \sum a'_{i2V} N_i^2. \quad (8)$$

By differentiating the equations devised by Hori and the author (here only carried out for  $\alpha$ ) one obtains:

$$d\alpha = \sum a_{i\alpha} dN_i, \quad (9)$$

$$d\alpha = \sum a_{i\alpha} dN_i + 2 \sum a'_{i\alpha} N_i dN_i. \quad (10)$$

From equation (9) it becomes apparent that  $d\alpha$  is a function of the changes in the chemical constitutions, while equation (10) is a function of both the chemical contents and their variations. Equation (9) proceeds as a special case from equation (10) because all coefficients of the type  $a'_{i\alpha} = 0$ . The author's investigations of the optical properties of knebelite indicate that the graph of the axial angle in the system  $\text{Fe}_2\text{SiO}_4$ - $\text{Mn}_2\text{SiO}_4$  has a minimum (i.e.  $d\alpha = 0$  at this point). Therefore  $d\alpha$  must be determined by the chemical contents as well as by their changes.

### The effect of cations on physical properties of knebelite and olivine

While Hori derived the equations for the refractive index and axial angle of the clinopyroxene group the present author determined the corresponding equations for minerals of the knebelite-olivine group. The material for the calcula-

*Table 1.* Recalculated analyses of knebelite and olivine minerals in molecular per cent. Nos. 1-10 from Henriques (1956), nos. 11-15 from Bowen and Schairer (1935).

Analy- sis no.	$\text{Fe}_2\text{SiO}_4$ mol.-%	$\text{Mn}_2\text{SiO}_4$ mol.-%	$\text{Mg}_2\text{SiO}_4$ mol.-%	Analy- sis no.	$\text{Fe}_2\text{SiO}_4$ mol.-%	$\text{Mn}_2\text{SiO}_4$ mol.-%	$\text{Mg}_2\text{SiO}_4$ mol.-%
1	85.82	8.30	5.89	9	52.95	44.49	2.56
2	82.61	14.46	2.92	10	45.26	51.06	3.68
3	50.84	19.67	29.49	11	—	—	100.00
4	69.65	25.60	4.74	12	40.8	—	59.2
5	62.48	27.80	9.72	13	67.4	—	32.6
6	58.07	30.60	11.33	14	86.1	—	13.9
7	57.50	35.40	7.10	15	100.0	—	—
8	54.22	40.33	5.45				

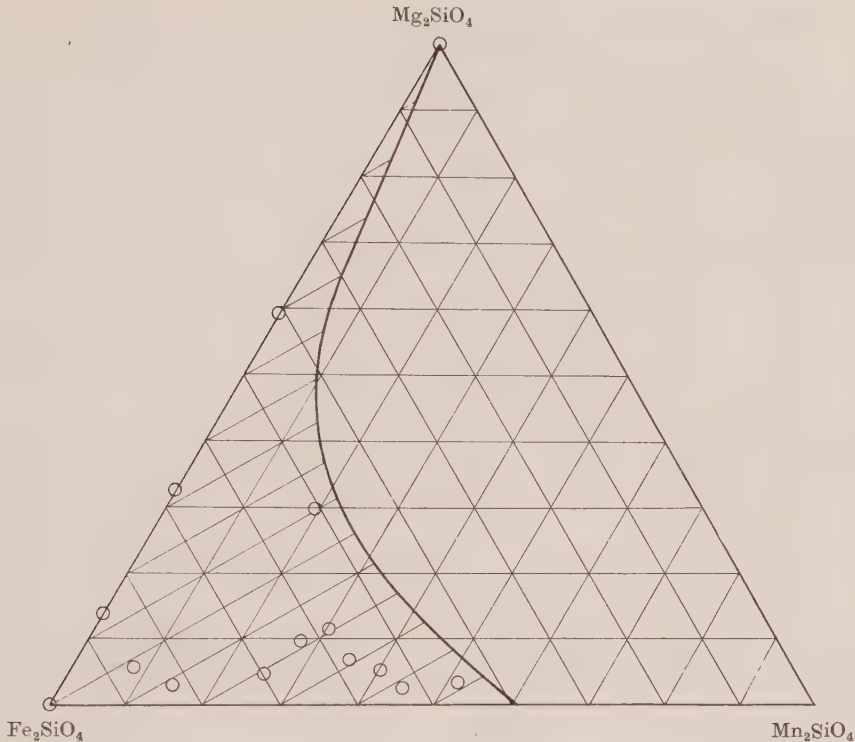


Diagram 1. Chemical composition of knebelite and olivine minerals 1-14 (Table 1).

Table 2. Optical properties and cell dimensions for knebelite according to equations of the type (1)-(4).

 $X_1 = \text{mol.-% Fe}_2\text{SiO}_4; X_2 = \text{mol.-% Mn}_2\text{SiO}_4; X_3 = \text{mol.-% Mg}_2\text{SiO}_4.$ 

$\alpha = (1.822 \pm 0.001) X_1 + (1.748 \pm 0.003) X_2 + (1.636 \pm 0.002) X_3$	(11)
$\beta = (1.863 \pm 0.001) X_1 + (1.790 \pm 0.002) X_2 + (1.651 \pm 0.001) X_3$	(12)
$\gamma = (1.873 \pm 0.001) X_1 + (1.794 \pm 0.003) X_2 + (1.669 \pm 0.002) X_3$	(13)
$2V_\alpha = (47.9 \pm 0.6) X_1 + (41.8 \pm 1.1) X_2 + (98.1 \pm 2.3) X_3$	(14)
$a_0 = (6.094 \pm 0.002) X_1 + (6.231 \pm 0.004) X_2 + (5.989 \pm 0.008) X_3$	(15)
$b_0 = (4.826 \pm 0.001) X_1 + (4.884 \pm 0.002) X_2 + (4.778 \pm 0.004) X_3$	(16)
$c_0 = (10.495 \pm 0.004) X_1 + (10.729 \pm 0.007) X_2 + (10.206 \pm 0.016) X_3$	(17)

tion of the regression equations was obtained from an investigation of the optical and chemical properties of knebelite  $(\text{Fe, Mn, Mg})_2\text{SiO}_4$  by the writer (1956).<sup>1</sup> Further hereto the refractive index values obtained by Bowen and

<sup>1</sup> In that paper on pages 262 and 264  $2V_\gamma$  should be corrected to  $2V_\alpha$ .



Table 3. Optical properties and cell-dimensions for knebelite according to equations of the type (5)–(8).

$X_1$  = mol.-%  $\text{Fe}_2\text{SiO}_4$ ;  $X_2$  = mol.-%  $\text{Mn}_2\text{SiO}_4$ ;  $X_3$  = mol.-%  $\text{Mg}_2\text{SiO}_4$ .

$\alpha = (1.811 \pm 0.022) X_1 + (0.012 \pm 0.022) X_1^2 + (1.732 \pm 0.015) X_2 + (0.049 \pm 0.019) X_2^2 + (1.647 \pm 0.019) X_3 - (0.011 \pm 0.019) X_3^2$		(18)
$\beta = (1.849 \pm 0.024) X_1 + (0.015 \pm 0.025) X_1^2 + (1.787 \pm 0.017) X_2 + (0.023 \pm 0.021) X_2^2 + (1.666 \pm 0.022) X_3 - (0.015 \pm 0.022) X_3^2$		(19)
$\gamma = (1.834 \pm 0.033) X_1 + (0.040 \pm 0.034) X_1^2 + (1.804 \pm 0.023) X_2 + (0.019 \pm 0.029) X_2^2 + (1.707 \pm 0.030) X_3 - (0.038 \pm 0.030) X_3^2$		(20)
$2V_\alpha = (24.1 \pm 49.3) X_1 - (24.8 \pm 51.2) X_1^2 + (51.1 \pm 44.6) X_2 + (0.3 \pm 44.9) X_2^2 + (136.0 \pm 21.3) X_3 - (87.5 \pm 31.2) X_3^2$		(21)
$\alpha_0 = (6.203 \pm 0.168) X_1 - (0.109 \pm 0.175) X_1^2 + (6.118 \pm 0.148) X_2 + (0.132 \pm 0.146) X_2^2 + (5.906 \pm 0.078) X_3 + (0.176 \pm 0.109) X_3^2$		(22)
$b_0 = (4.730 \pm 0.002) X_1 + (0.102 \pm 0.002) X_1^2 + (4.980 \pm 0.002) X_2 - (0.099 \pm 0.002) X_2^2 + (4.764 \pm 0.001) X_3 + (0.144 \pm 0.001) X_3^2$		(23)
$c_0 = (10.754 \pm 0.588) X_1 - (0.273 \pm 0.611) X_1^2 + (10.507 \pm 0.518) X_2 + (0.200 \pm 0.509) X_2^2 + (10.161 \pm 0.274) X_3 - (0.151 \pm 0.383) X_3^2$		(24)

Table 4. Refractive index of the end-members, observed and calculated values according to the equations (11)–(13) (Table 2).

	$\alpha$	$\beta$	$\gamma$
$\text{Fe}_2\text{SiO}_4$	$1.822 \pm 0.001$ $1.824^1$ $1.822^2$	$1.863 \pm 0.001$ $1.864^1$ $1.864^2$	$1.873 \pm 0.001$ $1.875^1$ $1.875^2$
$\text{Mn}_2\text{SiO}_4$	$1.748 \pm 0.003$ $1.78^1$ $1.77^3$	$1.790 \pm 0.002$ $1.805^1$ $1.807^3$	$1.794 \pm 0.003$ $1.82^1$ $1.825^3$
$\text{Mg}_2\text{SiO}_4$	$1.636 \pm 0.002$ $1.635^1$ $1.636^2$	$1.651 \pm 0.001$ $1.651^1$ $1.651^2$	$1.669 \pm 0.002$ $1.670^1$ $1.669^2$

<sup>1</sup> Winchell (1951).

<sup>2</sup> Bowen and Schairer (1935).

<sup>3</sup> Palache (1935).

Schairer (1935) for olivine minerals  $(\text{Fe, Mg})_2\text{SiO}_4$  synthesized by them have been used.

A greater number of carefully examined minerals from the olivine group could have been used in the investigation but the author on considering the difficulty of critically examining such heterogeneous material, decided to limit the investigation to the above-mentioned minerals, the recalculated analyses of which are presented in Table 1. According to Vegard's law there is an ap-

*Table 5.* Refractive index of knebelite and olivine minerals, observed and calculated values according to the equations (11)–(13) (Table 2).

No.	$\alpha$ obs	$\alpha$ calc	$\Delta \alpha$	$\beta$ obs	$\beta$ calc	$\Delta \beta$	$\gamma$ obs	$\gamma$ calc	$\Delta \gamma$
1	1.802	1.805	–0.003	1.843	1.845	–0.002	1.853	1.855	–0.002
2	1.803	1.806	–0.003	1.843	1.846	–0.003	1.851	1.855	–0.004
3	1.750	1.753	–0.003	1.784	1.786	–0.002	1.796	1.797	–0.001
4	1.792	1.794	–0.002	1.833	1.834	–0.001	1.842	1.843	–0.001
5	1.785	1.783	0.002	1.824	1.822	0.002	1.834	1.831	0.003
6	1.777	1.778	–0.001	1.818	1.817	0.001	1.828	1.826	0.002
7	1.782	1.783	–0.001	1.822	1.822	0.000	1.831	1.831	0.000
8	1.782	1.782	0.000	1.822	1.822	0.000	1.830	1.830	0.000
9	1.784	1.784	0.000	1.823	1.825	–0.002	1.830	1.833	–0.003
10	1.780	1.777	0.003	1.820	1.818	0.002	1.828	1.825	0.003
11	1.636	1.636	0.000	1.651	1.651	0.000	1.669	1.669	0.000
12	1.712	1.712	0.000	1.738	1.737	0.001	1.752	1.752	0.000
13	1.762	1.761	0.001	1.794	1.794	0.000	1.807	1.806	0.001
14	1.798	1.796	0.002	1.835	1.834	0.001	1.848	1.845	0.003
15	1.824	1.822	0.002	1.864	1.863	0.001	1.875	1.873	0.002

*Table 6.* Refractive index of knebelite and olivine minerals, observed and calculated values according to the equations (18)–(20) (Table 3).

No.	$\alpha$ obs	$\alpha$ calc	$\Delta \alpha$	$\beta$ obs	$\beta$ calc	$\Delta \beta$	$\gamma$ obs	$\gamma$ calc	$\Delta \gamma$
1	1.802	1.804	–0.002	1.843	1.844	–0.001	1.853	1.854	–0.001
2	1.803	1.804	–0.001	1.843	1.845	–0.002	1.851	1.853	–0.002
3	1.750	1.751	–0.001	1.784	1.786	–0.002	1.796	1.798	–0.002
4	1.792	1.792	0.000	1.833	1.833	0.000	1.842	1.841	0.001
5	1.785	1.781	0.004	1.824	1.821	0.003	1.834	1.830	0.004
6	1.777	1.777	0.000	1.818	1.816	0.002	1.828	1.825	0.003
7	1.782	1.781	0.001	1.822	1.822	0.000	1.831	1.830	0.001
8	1.782	1.782	0.000	1.822	1.822	0.000	1.830	1.830	0.000
9	1.784	1.785	–0.001	1.823	1.825	–0.002	1.830	1.832	–0.002
10	1.780	1.780	0.000	1.820	1.820	0.000	1.828	1.827	0.001
11	1.636	1.636	0.000	1.651	1.651	0.000	1.669	1.669	0.000
12	1.712	1.712	0.000	1.738	1.738	0.000	1.752	1.752	0.000
13	1.762	1.762	0.000	1.794	1.795	–0.001	1.807	1.807	0.000
14	1.798	1.797	0.001	1.835	1.834	0.001	1.848	1.845	0.003
15	1.824	1.823	0.001	1.864	1.864	0.000	1.875	1.874	0.001

proximately linear relationship between chemical content and the lengths of the unit cell within an isomorphous series. Consequently regression equations were also calculated for the unit cell lengths. The regression equations were solved with a digital computer (BESK) by the method of least squares in accordance with the Gauss elimination method. The average error was calculated in accordance with the formula:

$$\left( X_{i,i+2} \frac{V^2}{m-n} \right)^{\frac{1}{2}} \quad (11)$$

where  $X_{i,i+2}$  is the diagonal element belonging to  $X_i$  in the diagonal element

Table 7. Optic axial angle of knebelite according to equation (14) (Table 2).

No.	$2V_{\alpha}$ obs	$2V_{\alpha}$ calc	$\Delta 2V_{\alpha}$	No.	$2V_{\alpha}$ obs	$2V_{\alpha}$ calc	$\Delta 2V_{\alpha}$
1	50.7	50.4	0.3	6	52.1	51.7	0.6
2	48.1	48.5	-0.4	7	49.6	49.3	0.3
3	61.2	61.5	-0.3	8	47.6	48.2	-0.6
4	48.5	48.7	-0.2	9	45.6	46.5	-0.9
5	51.5	51.1	0.4	10	47.4	46.6	0.8

Table 8. Optic axial angle of knebelite according to equation (21) (Table 3).

No.	$2V_{\alpha}$ obs	$2V_{\alpha}$ calc	$2V_{\alpha}$	No.	$2V_{\alpha}$ obs	$2V_{\alpha}$ calc	$2V_{\alpha}$
1	50.7	50.9	-0.2	6	52.1	52.3	-0.2
2	48.1	48.1	0.0	7	49.6	49.4	0.2
3	61.2	61.2	0.0	8	47.6	48.2	-0.6
4	48.5	48.2	0.3	9	45.6	45.9	-0.3
5	51.5	51.4	0.1	10	47.4	47.0	0.4

Table 9. Unit cell lengths of knebelite, observed and calculated values according to the equations (15)-(17) (Table 2).

No.	$a_0$ obs	$a_0$ calc	$\Delta a_0$	$b_0$ obs	$b_0$ calc	$\Delta b_0$	$c_0$ obs	$c_0$ calc	$\Delta c_0$
1	6.100	6.100	0.000	4.828	4.829	-0.001	10.498	10.498	0.000
2	6.111	6.110	0.001	4.834	4.833	0.001	10.518	10.519	-0.001
3	6.091	6.090	0.001	4.824	4.823	0.001	10.454	10.456	-0.002
5	6.121	6.122	-0.001	4.836	4.837	-0.001	10.533	10.532	0.001
6	6.122	6.124	-0.002	4.837	4.838	-0.001	10.541	10.534	0.007
7	6.133	6.135	-0.002	4.843	4.843	0.000	10.556	10.557	-0.001
8	6.141	6.143	-0.002	4.847	4.847	0.000	10.569	10.574	-0.005
9	6.154	6.152	0.002	4.851	4.850	0.001	10.595	10.592	0.003
10	6.162	6.160	0.002	4.854	4.854	0.000	10.602	10.604	-0.002

of the inverse matrix and  $V$  "the vector of error". The large increase in the size of average error observed in the equations containing the terms  $\sum a_i N_i^2$  is probably due to the fact that too few determinations are available. In Tables 2 and 3 above the here derived equations for the refractive indices, for the axial angle and for the unit cell lengths are listed of knebelite and olivine minerals. The equations for the refractive indices were derived from the whole material, those of the axial angle and unit cell lengths solely from the knebelite. It should be observed that the derived equations are valid only for the examined part of the system  $\text{Fe}_2\text{SiO}_4\text{-Mn}_2\text{SiO}_4\text{-Mg}_2\text{SiO}_4$ . This is especially obvious by a comparison between the optical properties calculated from the formulas and the real values of the pure end-members tephroite  $\text{Mn}_2\text{SiO}_4$ , fayalite  $\text{Fe}_2\text{SiO}_4$ , forsterite  $\text{Mg}_2\text{SiO}_4$  (see Diagram 1 and Table 4). Partially calculated, partially determined values



Table 10. Unit cell lengths of knebelite, observed and calculated values according to the equations (22)–(24) (Table 3).

No.	$a_0$ obs	$a_0$ calc	$\Delta a_0$	$b_0$ obs	$b_0$ calc	$\Delta b_0$	$c_0$ obs	$c_0$ calc	$\Delta c_0$
1	6.100	6.100	0.000	4.828	4.828	0.000	10.498	10.499	–0.001
2	6.111	6.110	0.001	4.834	4.834	0.000	10.518	10.517	0.001
3	6.091	6.091	0.000	4.824	4.824	0.000	10.454	10.454	0.000
5	6.121	6.120	0.001	4.836	4.836	0.000	10.533	10.535	–0.002
6	6.122	6.121	0.001	4.837	4.837	0.000	10.541	10.536	0.005
7	6.133	6.134	–0.001	4.843	4.843	0.000	10.556	10.558	–0.002
8	6.141	6.143	–0.002	4.847	4.847	0.000	10.569	10.574	–0.005
9	6.154	6.154	0.000	4.851	4.851	0.000	10.595	10.592	0.003
10	6.162	6.161	0.001	4.854	4.854	0.000	10.602	10.602	0.000

Table 11. Changes in the optical properties and the unit cell lengths by an ionic substitution of 1 per cent in knebelite according to the equations (11)–(17) (Table 2).

Substituting ion		Substituted ion		
		$\text{Fe}^{2+}$	$\text{Mn}^{2+}$	$\text{Mg}^{2+}$
$\text{Fe}^{2+}$	$\delta \alpha \cdot 10^3$	—	0.74 (0.21)	1.86 (0.56)
	$\delta \beta \cdot 10^3$	—	0.73 (0.35)	2.12 (0.64)
	$\delta \gamma \cdot 10^3$	—	0.79 (0.24)	2.04 (0.64)
	$\delta 2V_\alpha$	—	0.06 (–0.06)	–0.50 (0.06)
	$\delta a_0 \cdot 10^3$	—	–1.37	1.05
	$\delta b_0 \cdot 10^3$	—	–0.57	0.48
	$\delta c_0 \cdot 10^3$	—	–2.34	2.89
$\text{Mn}^{2+}$	$\delta \alpha \cdot 10^3$	–0.74 (–0.21)	—	1.12 (0.35)
	$\delta \beta \cdot 10^3$	–0.73 (–0.35)	—	1.39 (0.29)
	$\delta \gamma \cdot 10^3$	–0.79 (–0.24)	—	1.25 (0.40)
	$\delta 2V_\alpha$	–0.06 (–0.06)	—	–0.56 (0.12)
	$\delta a_0 \cdot 10^3$	1.37	—	2.42
	$\delta b_0 \cdot 10^3$	0.57	—	1.06
	$\delta c_0 \cdot 10^3$	2.34	—	5.24
$\text{Mg}^{2+}$	$\delta \alpha \cdot 10^3$	–1.86 (–0.56)	–1.12 (–0.35)	—
	$\delta \beta \cdot 10^3$	–2.12 (–0.64)	–1.39 (–0.29)	—
	$\delta \gamma \cdot 10^3$	–2.04 (–0.64)	–1.25 (–0.40)	—
	$\delta 2V_\alpha$	0.50 (–0.06)	0.56 (–0.12)	—
	$\delta a_0 \cdot 10^3$	–1.05	–2.42	—
	$\delta b_0 \cdot 10^3$	–0.48	–1.06	—
	$\delta c_0 \cdot 10^3$	–2.89	–5.24	—

for refractive index, axial angle and unit cell lengths as well as divergencies between calculated and determined values are given in Tables 5, 6, 7, 8, 9, 10.

Variations in the optical properties and the unit cell lengths caused by an ionic substitution of 1 per cent in knebelite, calculated in accordance with the equations (11)–(17) (Table 2) are to be found in Table 11. Hori's values for a

Table 12. Chemical composition (in mol.-%) of knebelite and olivine as a function of the refractive indices.

$$\begin{aligned} [\text{Fe}] &= - (8.53 \pm 2.83) - (1.55 \pm 18.68) \alpha - (14.22 \pm 13.28) \beta + (20.65 \pm 20.95) \gamma \\ [\text{Mn}] &= (10.59 \pm 2.18) - (36.67 \pm 14.40) \alpha + (84.62 \pm 10.23) \beta - (54.12 \pm 16.14) \gamma \\ [\text{Mg}] &= - (1.06 \pm 2.28) + (38.21 \pm 15.09) \alpha - (70.40 \pm 10.73) \beta + (33.48 \pm 16.92) \gamma \end{aligned}$$

comparable substitution for clinopyroxenes are given in brackets. If a comparison be made the changes in refractive index brought about by substitution of  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Mg}^{2+}$  into clinopyroxenes and olivine minerals respectively it is found that the changes are essentially greater for the olivine group than for the clinopyroxenes (minimum 2.1 and maximum 4.8 times greater). This becomes also apparent on studying the available optical literature. For the present, at least, it does not seem suitable taking due consideration to the rather limited material investigated, to discuss here the connexion between crystallographic structure and optical properties. When the regression equations also contain the molecular fractions (Table 3), no simple scheme can be devised that shows the change in the physical properties caused by the substitution of one ionic type by another, as in this case the amount of the change, as previously noted, is a function of both the molecular proportions and their changes.

Attempts were also made to derive regression equations for chemical composition as a function of the refractive indices ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) of the minerals, but with a negative result, as the average error attached to each coefficient is often greater than the coefficient. This becomes apparent from the equations (Table 12).

## Results

1. When physical properties are correlated with chemical composition in an isomorphous series, where the relationship between physical properties and chemical composition is not linear, a better agreement will be received by using equations of second degree of the type (5)–(8), page 306.

2. Regression equations for chemical composition as a function of physical properties are usually not valid because the average error attached to each coefficient will be of the same magnitude as the coefficient.

## ACKNOWLEDGEMENTS

The author wishes to convey his thanks to Prof. F. E. Wickman, for his critical reading of the manuscript, and to Dr. K. Arle and Mr. L. Jansson for mathematical collaboration.

## REFERENCES

- BOWEN, N. L., and SCHAIRER, J. F. (1935), Olivines. *Am. J. Sc.*, Ser. V, *XXIX*, 195–197.  
HENRIQUES, C. Å. (1956), Optical and physical properties of knebelite. *Arkiv f. Mineralogi och geologi* 2, 255–269.

- HESS, H. H. (1949), Chemical composition and optical properties of common clinopyroxenes. Part I. *Am. Min.* 34, 621-666.
- HORI, F. (1954), Effects of Constituents Cations on the Optical Properties of Clinopyroxenes. *Scientific Papers of the College of General Education, University of Tokyo*, IV, 71-83.
- PALACHE, CH. (1935), The minerals of Franklin and Sterling Hill, Sussex County, New Jersey. *U.S. Geol. Sur., Prof. Pap.*, 180, 76.
- WINCHELL, A. N. and WINCHELL, H. (1951), *Elements of Optical Mineralogy. Part. II.* Fourth edition. New York, 499.

Tryckt den 15 oktober 1957

Uppsala 1957. Almqvist & Wiksells Boktryckeri AB





## Jagoite, a new lead-silicate mineral from Långban in Sweden

By RAGNAR BLIX, OLOF GABRIELSON and FRANS E. WICKMAN

### Introduction

The Långban mines are famous for the large number of lead-silicate minerals found there. So far, hyalotekite, ganomalite, nasonite, kentrolite, melanotekite, barysilite, margarosanite, molybdophyllite, and roebingite have been described. In this paper a tenth lead silicate is described, which, as far as we know, is new to science. We have called it *jagoite* in honour of the well-known mineral collector Mr. John B. Jago, San Francisco, California, who has shown an enthusiastic interest in the Långban minerals, and through generous donations of funds has made possible an intensive study of the Långban minerals at this museum.

### Occurrence

Jagoite is a rare mineral which was discovered around 1943 in hematite ore in the stope "Canberra" together with melanotekite, quartz, and a mixture consisting of a not yet identified mineral and quartz. Jagoite occurs as fine-grained micaceous aggregates of plates and is commonly surrounded by a zone of black melanotekite.

### X-ray crystallography

We have not been able to find any crystals with well-developed faces and we have therefore used X-ray methods exclusively. A Laue photograph taken perpendicular to a plate showed that the Laue-symmetry group is  $\bar{3}$ , i.e. the mineral is trigonal.

Oscillation, rotation, and equi-inclination photographs were taken with unfiltered copper radiation, using the *c*- and *a*-axes as rotation axes. The quality of the photographs was rather poor on account of the easiness with which the plates of jagoite are deformed.

The hexagonal unit cell has the dimensions:  $a = 8.65 \pm 0.03$  Å and  $c = 33.5 \pm 0.1$  Å. No systematic extinctions could be observed. This means that the possible space groups should be  $P3$  (No. 143) and  $P\bar{3}$  (No. 147).

The powder pattern of jagoite is shown in Table 1. It was obtained using a Debye-Scherrer camera (diameter 57.3 mm) and Ni-filtered copper radiation. No effort was made to prevent the development of a preferred orientation of the platy powder on the glass fiber. We have not thought it worth while to index

*Table 1.* Powder pattern of jagoite. Ni-filtered Cu radiation.

<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
5.6	2	1.93	1
4.16	5	1.85	2
3.40	10	1.700	2
3.10	2	1.654	2
2.99	5	1.620	2
2.80	8	1.604	2
2.60	3	1.553	3
2.50	4	1.479	1
2.47	3	1.431	1
2.34	2	1.398	1
2.11	2	1.380	1
2.06	3	1.331	1

the lines observed because the *c*-axis of jagoite is so large that it is always possible to find at least one reflection with a suitable *d*-value.

### Physical and optical properties

Jagoite has perfect basal cleavage, {0001}, and has a hardness of 3. The specific gravity is 5.43 as determined with a pycnometer. The luster is vitreous and shining on cleavage surfaces. The colour is yellow-green and the streak yellow. The mineral is not fluorescent under ultraviolet light.

In transmitted light under the microscope jagoite is light green. It is uniaxial with optical negative (−) character. The refringence is very high (around 2.0 according to a measurement by Nikitin's method); this is in agreement with what has been found in other lead silicates. The birefringence is intermediate (0.025). The mineral is nonpleochroic.

### Chemical composition

The chemical analysis made by one of us (R. B.) is shown in Table 2. The unit cell volume is 2170 Å<sup>3</sup> and the specific gravity is 5.43. The molecular weight of the unit cell is consequently 7102. This value has been used in calculating the figures in column 2 of Table 2.

It might be remarked that the oxidation state of iron was tested, and that no trace of ferrous iron could be detected. The mineral was tested for "superoxide" oxygen in a special apparatus but with negative result.

The formula of jagoite derived from the chemical analysis is



This tentative formula will indicate that electroneutrality is obtained by substitution of univalent cations for some of the large bivalent ones, bivalent cations for some of the trivalent ones, and beryllium and probably also aluminium for some of the silicon atoms.



Table 2. The chemical composition of jagoite.

1. The chemical analysis of jagoite (R. Blix).
2. The number of atoms in the hexagonal unit cell.
3. Suggested distribution of atoms of different sizes.
4. Ideal cell content.

	1		2	3	4
SiO <sub>2</sub>	22.35	Si	26.40	26.74	27
BeO	0.12	Be	0.34		
Al <sub>2</sub> O <sub>3</sub>	0.50	Al	0.70		
Fe <sub>2</sub> O <sub>3</sub>	7.00	Fe <sup>3+</sup>	6.22	8.06	8
TiO <sub>2</sub>	0.10	Ti	0.09		
MgO	0.60	Mg	1.05		
FeO	nil	Fe <sup>2+</sup>	0.00	24.11	24
MnO	0.88	Mn	0.88		
CaO	0.65	Ca	0.82		
PbO	64.26	Pb	20.45	7.84	8
Na <sub>2</sub> O	0.61	Na	1.40		
K <sub>2</sub> O	0.37	K	0.56		
Cl	3.25	Cl	6.50	83.87	84
H <sub>2</sub> O (> +105°C)	0.17	OH	1.34		
H <sub>2</sub> O (< +105°C)	0.19				
F	nil	F	0.00		
O	nil	O			
	101.05				
Less O for Cl . . . .	0.73				
	100.32				

It seems plausible to regard jagoite as a phyllosilicate. Owing to the fact that we have only one find of jagoite, we have no idea about the possible variations in its chemical composition, and can only hope that new occurrences will be discovered.

#### SUMMARY

Jagoite, (Pb,Ca,Mn,Na,K)<sub>24</sub>(Fe<sup>3+</sup>,Al,Mg)<sub>8</sub>(Si,Al,Be)<sub>27</sub>O<sub>84</sub>(OH,Cl)<sub>8</sub>, is a hexagonal mineral with unit cell lengths  $a = 8.65 \pm 0.03$  Å,  $c = 33.5 \pm 0.1$  Å. The probable space groups are  $P3$  and  $P\bar{3}$ . Physical and optical properties are given in the special section and the powder pattern given in Table 1.

Tryckt den 15 oktober 1957

Uppsala 1957. Almqvist & Wiksells Boktryckeri AB



## Alkaline rocks and carbonates of alkalies, calcium and magnesium

By N. SUNDIUS

With 7 figures in the text

Because of a note of P. J. Holmquist in his paper about synthesis of perowskite and pyrochlor minerals, stating that calcium carbonate is dissolved in a soda melt in considerable amounts (1), Dr. A. Bygdén, at the laboratory of the Geol. Survey of Sweden, made in about 1938 on my request some melts of mixtures of the alkali carbonates and  $\text{CaCO}_3$ . It was stated that both potassium and sodium carbonate form homogeneous and low melting double salts with  $\text{CaCO}_3$  with the molecular ratio of 1:1. The experiments were prompted by questions which arose from a study of the so-called "lime granites" in Sweden (2), but the work was not then completed.

Later the writer found that the systems  $\text{Na}_2\text{CO}_3\text{--CaCO}_3$  and  $\text{K}_2\text{CO}_3\text{--CaCO}_3$  had been systematically investigated by P. Niggli in 1916 (3), who also referred to earlier observations. Among others, Le Chatelier had as early as 1894 prepared the two double carbonates, and he gives  $790^\circ\text{C}$  as the temperature of formation for them both.

The results from the melting experiments by Niggli are summarized in the two equilibrium diagrams of Fig. 1, in which the one with potassium carbonate is incomplete. To the diagrams the following is to be added.

Both sodium and potassium carbonate form double salts with  $\text{CaCO}_3$  the ratio 1:1. The melting point of both is about  $815^\circ\text{C}$ . All mixtures between these compounds and the pure alkali carbonates melt easily and form clear and mobile melts without appreciable dissociation at one atm.  $\text{CO}_2$ . From pure  $\text{Na}_2\text{CO}_3$  to about 20 mol. %  $\text{CaCO}_3$  the loss of  $\text{CO}_2$  is very small. At 32 mol. %  $\text{CaCO}_3$  and  $968^\circ\text{C}$  it was found to be less than 2% of the whole  $\text{CO}_2$  content. In mixtures of 30–40 mol. %  $\text{CaCO}_3$  and at  $930^\circ\text{C}$  it is still less than 1.2% and at 58 mol. %  $\text{CaCO}_3$  and  $875^\circ\text{C}$  it is only little more than 1–2%.

If the temperature is raised, the mixtures in the soda–lime system begin to boil with the dissociation of the carbonates. As an example of the boiling temperature, some of Niggli's data are given. At 24 mol. %  $\text{CaCO}_3$  no boiling occurs at  $1000^\circ\text{C}$ . At 39 mol. %  $\text{CaCO}_3$  boiling is observed at  $970^\circ\text{C}$  but not at  $930^\circ\text{C}$ . In a mixture of 75 mol.  $\text{CaCO}_3$ ,  $\text{CaO}$  is formed between  $880^\circ$  and  $911^\circ\text{C}$ .

The relations are similar in the  $\text{K}_2\text{CO}_3\text{--CaCO}_3$  system in the part investigated (up to 50 mol. %  $\text{K}_2\text{CO}_3$ ).

In both systems deep eutectics occur between the alkali carbonate and the double salt, in the sodium–calcium system at about  $785^\circ\text{C}$  and 63 mol. %  $\text{Na}_2\text{CO}_3$ , and in the



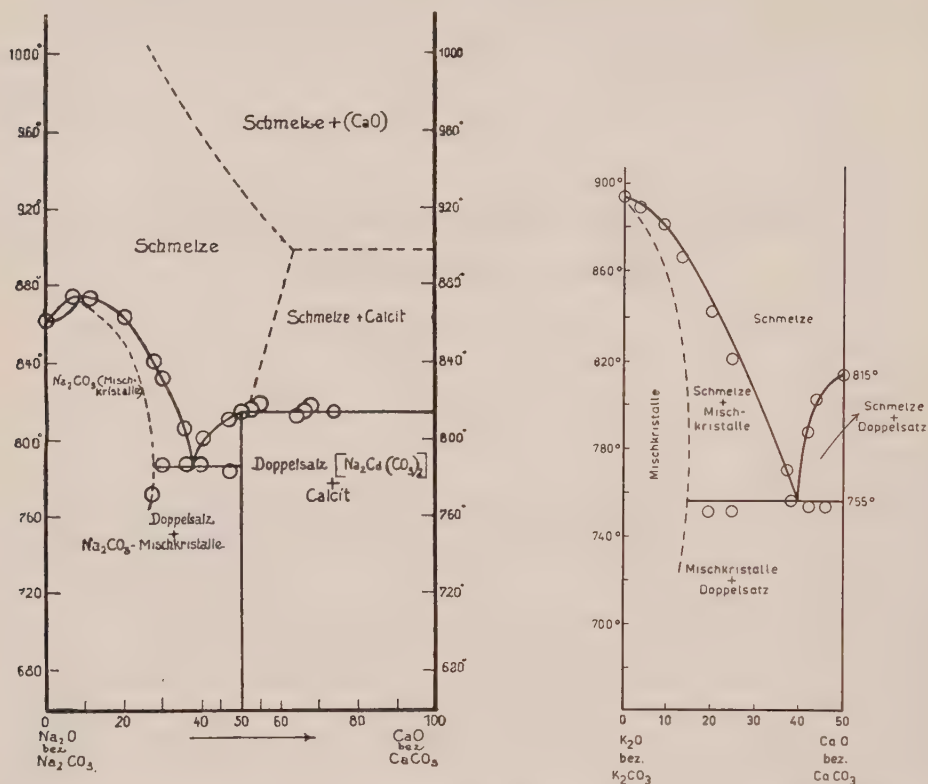


Fig. 1. Equilibrium diagrams of the systems  $\text{Na}_2\text{CO}_3$ - $\text{CaCO}_3$  and  $\text{K}_2\text{CO}_3$ - $\text{CaCO}_3$  at one atm.  $\text{CO}_2$  pressure, according to P. Niggli. Mol. %.

potassium system at  $755^\circ\text{C}$  and about 61 mol. %  $\text{K}_2\text{CO}_3$ . There is partial solubility of the double carbonates in the alkali carbonates.

On the lime side of the double carbonates the relations are somewhat more complicated. According to the diagram of the  $\text{Na}_2\text{CO}_3$ - $\text{CaCO}_3$  system the double carbonate melts, and a mixture of this compound and  $\text{CaCO}_3$  extends up to the dissociation boundary.

Niggli did not get the double salt  $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$  in his experiments. However a mineral of this composition (shortite, cf. below) is known from nature. A double salt between  $\text{K}_2\text{Ca}(\text{CO}_3)_2$  and  $\text{CaCO}_3$  was suggested by Niggli. In reality the compound  $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$  was found by C. Kröger, K. W. Illner and W. Graesser (4) in a study of the  $\text{K}_2\text{CO}_3$ - $\text{CaCO}_3$  system of 1943. As there is some dissociation in the  $\text{CaCO}_3$ -rich part of the diagram at one atm.  $\text{CO}_2$ , the study was made under a pressure of 50 atm.  $\text{CO}_2$ . The resulting diagram is shown in Fig. 2. The new compound  $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$  has a melting point of  $835^\circ\text{C}$ . The eutectic between it and  $\text{K}_2\text{Ca}(\text{CO}_3)_2$  lies at about  $790^\circ\text{C}$  and 60 mol. %  $\text{CaCO}_3$ .

A complementary investigation of the ternary system  $\text{Na}_2\text{CO}_3$ - $\text{K}_2\text{CO}_3$ - $\text{CaCO}_3$  up to  $900^\circ\text{C}$  at one atm.  $\text{CO}_2$  was published by Niggli in a paper of 1919 (5).<sup>1</sup> The equi-

<sup>1</sup> My attention was kindly directed to this paper by Prof. H. von Eckermann.

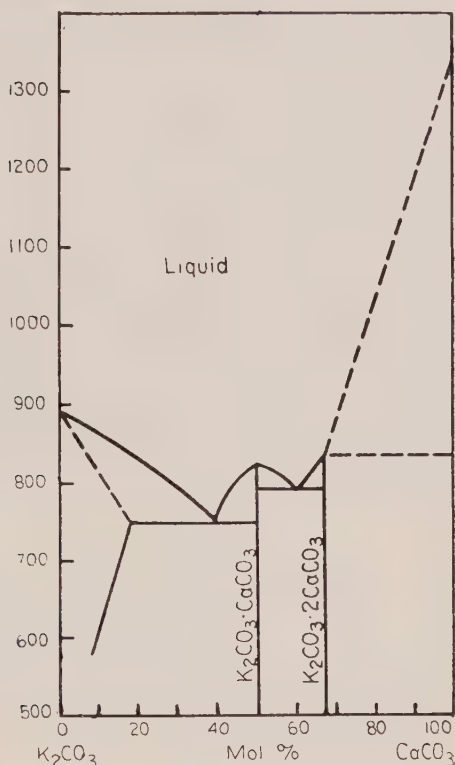
$\text{K}_2\text{CO}_3\text{--CaCO}_3$ 


Fig. 2. Equilibrium diagram of the system  $\text{K}_2\text{CO}_3$  and  $\text{CaCO}_3$  at 50 atm.  $\text{CO}_2$  pressure, according to C. Kröger, K. W. Illner and W. Graeser. Mol. %.

Equilibrium diagram is shown in Fig. 3. The double carbonates  $\text{Na}_2\text{Ca}(\text{CO}_3)_2$  and  $\text{K}_2\text{Ca}(\text{CO}_3)_2$  form according to him a complete series of solid solutions and the eutectic curve between this series and the  $(\text{Na}_2\text{K}_2\text{Ca})\text{CO}_3$  solid solutions has its lowest point at about  $693^\circ\text{C}$ .<sup>1</sup>

The diagram does not contain the double salts  $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$  and  $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ . Possibly they cannot be realized at one atm.  $\text{CO}_2$ , but the presence of them at a somewhat higher pressure may essentially alter the aspect of the upper part of the diagram.

The double carbonate  $\text{Na}_2\text{Ca}(\text{CO}_3)_2$  has also been prepared through reaction in solids by R. Jaggitsch, B. Jacobsson and S. Rolin at  $650^\circ$  and  $700^\circ\text{C}$  (6).

By water the double carbonates are easily decomposed into a solution of alkali carbonate and solid  $\text{CaCO}_3$ , and  $\text{K}_2\text{Ca}(\text{CO}_3)_2$  may be somewhat deliquescent in air.

Other double carbonates of interest in this connection are  $\text{Na}_2\text{Mg}(\text{CO}_3)_2$  and

<sup>1</sup> In a mixture of similar parts by weight of both eutectics between the alkalicarbonates and the double salts (mol. ratio  $\text{Na}_2\text{CO}_3 = 33,7$ ,  $\text{K}_2\text{CO}_3 = 27,4$ ,  $\text{CaCO}_3 = 38,9$ ) Dr. R. Blix in the laboratory of the Min. Dept. of the Swedish Museum of Natural History in Stockholm made at my request a preliminary melting test. Signs of melting were observed at  $660^\circ\text{C}$ . At  $700^\circ\text{C}$  the mixture had melted to a clear and mobile melt. Possibly the difference from Niggli's diagram ( $693^\circ$  and  $777^\circ\text{C}$ ) may at least partly be due to the fact that the experiment of Blix was made in air and, further, to some small quantity of water in the carbonates used. No free lime could be shown in the crystallized melt optically or by White's reagent.

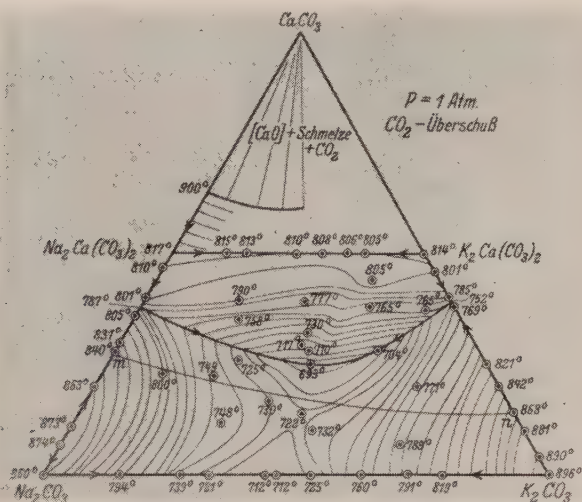


Fig. 3. Equilibrium diagram of the system

$\text{Na}_2\text{CO}_3\text{--K}_2\text{CO}_3\text{--CaCO}_3$   
according to P. Niggli, 1919.  
Mol. %.

$\text{K}_2\text{Mg}(\text{CO}_3)_2$ . Because of the low dissociation temperature of  $\text{MgCO}_3$  they may not be able to form at one atm.  $\text{CO}_2$  pressure. In water solution  $\text{Na}_2\text{Mg}(\text{CO}_3)_2$  has been prepared by A. de Schulten (7), G. von Knorre, W. Eitel and W. Skaliks (8). The two latter (8) obtained both the sodium and the potassium double salts in melts with the mol. mixture 1:1 under  $\text{CO}_2$  pressures of 1240 kg/cm<sup>2</sup> for the former and 1200 atm. for the potassium compound. The melting point of  $\text{Na}_2\text{Mg}(\text{CO}_3)_2$  was determined to be 677°C, or 138° lower than that of the corresponding sodium-calcium compound. No determination was made for  $\text{K}_2\text{Mg}(\text{CO}_3)_2$ , presumably on account of the difficulty in crystallizing the melt.

Niggli refers to an earlier work of Le Chatelier (9) according to which the double carbonates  $\text{Na}_2\text{Ba}(\text{CO}_3)_2$  and  $\text{Na}_2\text{Sr}(\text{CO}_3)_2$  should be formed in melts with the mol. ratio of 1:1. A later test by W. Eitel [10] did not corroborate this. Both  $\text{BaCO}_3$  and  $\text{SrCO}_3$  form mixtures with  $\text{Na}_2\text{CO}_3$ , with eutectics at 716°C and 80 mol. %  $\text{Na}_2\text{CO}_3$  in the case of the Ba-carbonate, and 702°C and 83 mol. %  $\text{Na}_2\text{CO}_3$  in the  $\text{SrCO}_3\text{--Na}_2\text{CO}_3$  system.

Indeed, though the named double carbonates and the equilibrium relations in the ternary carbonate system  $\text{Na}_2\text{CO}_3\text{--K}_2\text{CO}_3\text{--CaCO}_3$  have been known for a long time, they have attracted little attention from mineralogists and geologists, and seem to be unknown to most of them. One reason for this is that the double salts have little chance to be formed or to survive in the superficial parts of the crust on account of their easy decomposition by water. One of the double salts,  $\text{K}_2\text{Ca}(\text{CO}_3)_2$  has been found in ashes of forest fires and has received the name *fairchildite* (11). It is unstable in air and is changed to  $3\text{K}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  (Bütschliite) and free  $\text{CaCO}_3$ . Another double salt, not, however, obtained in the melting tests, is *shortite* ( $\text{Na}_2\text{Ca}_2(\text{CO}_3)_3$ ) (11), the sodium analogy to the potassium-double salt found by Kröger, Illner and Graeser. It has been observed in drillings together with montmorillonite in an Eocene clay in Wyoming at a depth of 1258–1805 feet.

None the less, double carbonates of the named or related types may exist in magmatic solutions, and they have probably played an important role in the production of carbonatites and  $\text{SiO}_2$ -undersaturated alkaline rocks.



### Carbonates in the magma

The magmas contain as chief volatile constituents  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . Accordingly equilibrium must be established in deep-seated magmas between silicates on the one hand and hydratized compounds and carbonates on the other. Carbonates of calcium, magnesium and the alkalis may be formed, and thus the possibility of the formation of double salts of the carbonates must be admitted. Normally the carbonate content will be low, and probably the chance that it would crystallize during cooling is small. Because of the low melting of the double carbonates and their mixtures with calcium or alkali carbonates, they must enter in the residual solution here also water, alkali hydrates,  $\text{SiO}_2$ , and other substances (presumably as  $\text{Al}_2\text{O}_3$  compounds) are concentrated. With decreasing temperature the double carbonates may be decomposed, and their alkali contents may enter into alkali feldspar and micas, while the calcium and magnesium may enter into late formed hornblende, epidote or they may crystallize as carbonates. The quantities of the carbonates in the residual solution must normally be small. But if there are differentiation processes causing an assembling of carbonates and hydrates in some parts of the magma chamber, as for instance through squeezing or through the rise of light substances to the upper part of the magma, fractions of them could be formed in which under-saturation of  $\text{SiO}_2$  is produced and where the content of alkalis is high. In this way carbonate and alkali-rich parts of the magma could be formed. This is the same theory that has been proposed by Bowen (12), except that the role played by the carbonates is not considered by him. But it seems absurd to deny the possibility that alkaline rocks can be formed by fractional processes of this kind. The subject will be further discussed in the chapter about the lime-syenites and pegmatites.

A more effective process of separating the carbonate solution from the silicates in a magma should be that of a liquation but little is known concerning this possibility.

### The syntectic theory of Daly

The feldspathoid-bearing rocks show many variations in different localities but a very general property is the occurrence in them of  $\text{CO}_2$ -bearing minerals such as carbonates and cancrinite, and of silicate derivatives from calcium carbonate, such as vesuvianite, melilite, scapolite, and others. Indeed the combination of carbonatites and nepheline syenites is so common that the conclusion lies near at hand that the building of the latter presupposes the presence of carbonates. The general presence of carbonates in connection with alkaline rocks was the basis for the very interesting theory of Daly on the syntexis of a magma and carbonate rocks. In his papers concerning this theme (13) he has discussed the reactions that presumably will take place, if a limestone or dolomite is invaded and assimilated by a magma. Briefly they are the following : (1)  $\text{CaCO}_3$  and dolomite act as a flux when dissolved in the magma in that they diminish the viscosity and aid the reactions and the gravitative movements of the crystals in the magma. (2) The carbonates are partly dissociated and the  $\text{CaO}$  and  $\text{MgO}$  made free contribute to the desilication of the magma. The new-formed  $\text{Ca-Mg}$  silicates tend to sink and the residue to be enriched in alkalis and aluminium. (3) The liberated  $\text{CO}_2$  forms compounds with the alkalis, if free  $\text{SiO}_2$  is absent, and the alkali- $\text{CO}_2$  compounds tend to rise to a higher level. (4) When calcium carbonate and alkali feldspar are heated together, the latter is decomposed and forms free alkali oxides.

Of these reactions, the last-named (4) is the same reaction that occurs in cement kilns, where the alkalies for the greater part are driven up to the smoke stack, a minor part being retained as sulphates and sulphites in the clinker and in the lining of the kiln. No doubt a decomposition of this kind may occur in a deep-seated magma, if carbonate rocks are assimilated; however the alkali-oxides may not escape, but may rather combine with  $\text{CO}_2$  and form carbonates, whereas the residue of the feldspars together with  $\text{CaO}$  and  $\text{MgO}$  form silicates.

A difficulty in the reasoning of Daly that has not been discussed is how the calcium and magnesium carbonates can be dissolved in the magma. It is also apparent that the limestones and dolomites that accompany the nepheline syenites have been in solution in its mother magma, and the quantity of carbonate can be rather great. Calcium carbonate has a rather high melting point, according to Boeke (14)  $1289^\circ\text{C}$  at 110 atm. pressure of  $\text{CO}_2$  and it is very slightly soluble in alkalie but not carbonatic solutions.

For this question the information gained from the investigations of the carbonate systems as given above, is of importance. Our knowledge of the relations in these systems is still incomplete, but the facts known allow of the general statement that the alkali carbonates formed during the syntectic reactions in the magma will combine with  $\text{CaCO}_3$  and  $\text{MgCO}_3$  to form double salts with low melting points. Thus the dissolving media for  $\text{CaCO}_3$  and  $\text{MgCO}_3$  are the alkali carbonates. What composition the carbonate mixture in the magma will have is impossible to decide, and it may vary in different cases. If the supply of calcium-magnesium carbonate is great and the temperature in the magma high, the ratio of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  in the solution will tend to exceed that of the alkali carbonates, while at a low temperature the contrary may be the case.

It must be a rather peculiar derivative of magma that is formed if reactions of this kind are effective. The resulting solution will be a chiefly carbonatic one, rich in alkalies and highly mobile. The freezing temperature must be low, the lower boundary lying at about that of the eutectic in the ternary carbonate system  $\text{Na}_2\text{CO}_3$ – $\text{K}_2\text{CO}_3$ – $\text{CaCO}_3$  or somewhat lower, reasonably at about  $600$ – $650^\circ\text{C}$ . Some water from the original magma and the assimilated carbonate rock—especially if the latter was argillaceous—may be present.

### The mother solution of the Alnö alkaline rocks

It may have been somewhat of a shock for geologists when Högbom 1895 in his paper about the classical Alnö alkaline rocks (15) stated that the limestone associated with the nepheline syenite was magmatic in the sense that it had been dissolved in the magma and crystallized from it. Since that time, so many instances of the same kind have been described that at present the magmatic nature of the carbonate rocks in the sense claimed by Högbom probably may be generally adopted.

Thanks to the detailed and valuable work of H. von Eckermann (16) the Alnö alkaline rock complex is perhaps the best known one in the world, and it is of interest to quote his conclusions about the mother magma of the rocks. The latter are according to him only to a minor extent products of solidification of primary magma and are chiefly the result of metasomatic changes (finitization) in the environs around the magma diatrema. A huge amount of alkalies, chiefly potash, migrated outwards from the central part that is occupied by limestone (sövite) and a great number of carbonate dikes invaded the finitized rocks.

On the basis of his studies, von Eckermann characterises the mother magma as a "magmatic melt, or rather liquid", that "is suggested to have been a high tensional one of low temperature (400–600°C), consisting of mainly carbonates, predominatingly potassic and containing as additional essential components: lime, magnesia, alumina, iron, titanium and phosphorus, as well as free carbon dioxide, much fluorine and comparatively little water" (17). According to the size of the central limestone, and with due regard to the many carbonate dikes and the calcium in melilite and wollastonite in the district, calcium and magnesium carbonate may have made up an essential part of the solution. The dominating constituents of the Alnö solution may, roughly speaking, have formed a mixture of double carbonates and alkali carbonates, the molecular proportion of alkalies being greater than that of calcium and magnesium. This mixture must have had a low freezing temperature. If, as perhaps may be possible, the mixture was approximately that of the eutectic of  $K_2(CO_3)_3$ ,  $K_2Ca(CO_3)_2$  and  $K_2Mg(CO_3)_2$ , the melting point would have been lower than 752°C, the eutectic temperature in the system  $K_2CO_3$ – $CaCO_3$ . As some  $Na_2CO_3$  was present, the temperature may even have been somewhat lower. Furthermore, as the magma has contained much fluorine and carbon dioxide and moderate amounts of water, the real temperature may have been further lowered. The upper temperature of 600°C, deduced by von Eckermann from mineral reactions seems not improbable according to the calculation above. Also phosphorus and titanium, if they are present in alkali compounds, act as fluxes.

In the alkaline district, barium is present in unusual amounts. Barium is known to follow potassium in rocks. It is possible that it too was contained in the magma solution as carbonate. The behavior of  $BaCO_3$  in mixtures with  $K_2CO_3$  is still unknown, but in mixtures with  $Na_2CO_3$  it forms a low melting eutectic (melting point 702°C).

### **Lime syenites and calcite bearing pegmatite**

Rather many occurrences of these rocks are known from Sweden (2). Of old the first named have been called "lime granites" because they occur as modifications of granites, but this name is misleading as they are always characterized by absence or scarcity of quartz. Unfortunately the rocks in most cases are known only from loose boulders. The cases where they have been observed in situ are few, and in reality, the relations to the country rocks have been studied only at three localities. These are a pegmatite at Skarpö (18), an island in the neighbourhood of the town Vaxholm, a lime syenite in the southern part of Stockholm (Skåne street) (2), and a pegmatite at Getlycke in southern Bohuslän (19).

According to the description by Högbom, the calcite bearing pegmatite on Skarpö formed an irregular patch on the bottom of a feldspar quarry and had an area of only some square metres, with indistinct boundaries against the surrounding normal graphic pegmatite. The pegmatite variety in this patch was the famous graphic feldspar containing numerous cavities of the same form and distribution as the quartz in a usual graphic feldspar (Fig. 4). On account of this it was long considered to be a graphic feldspar from which the quartz had been dissolved, leaving the feldspar intact, until it was shown that the filling substance of the cavities had been calcite, remnants of which also could be found. Both plagioclase and microcline perthite were developed in the same manner, though the latter was dominating. The whole syenitic modification of the pegmatite consisted of coarse feldspars of this kind.



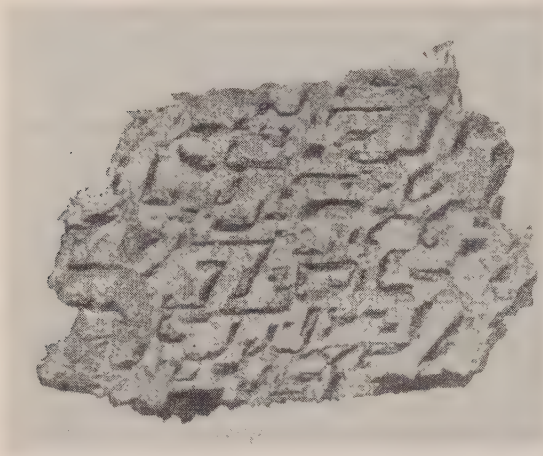


Fig. 4. Specimen of Skarpö-microcline perthite with cavities after dissolved calcite. Nat. size.

At Getlycke the calcite-bearing rock forms a border along the one boundary of a pegmatite lens, mapped in detail by R. Looström (Fig. 7). It has a unilateral building with a usual quartz-feldspar-biotite pegmatite in the main northern part. Outside of it follow three different zones (B–D), indicating a differentiation in the lens and a gradually decreasing freezing temperature in the zones, the lowest temperature being found in the outermost border (D), which consists of a reddish microcline perthite enclosing calcite grains in a graphic manner though somewhat more sparse than at Skarpö.<sup>1</sup>

The lime syenite found in Stockholm occurs in ordinary grey Archean granite and forms an oval area of about  $15 \times 7$  m. The length can be somewhat greater as the extreme end was not exposed in the one direction. Where the boundary of the lime syenite towards the granite could be seen, it was rather definite but did not have the character of a sharp contact. The lime syenite was a grey or secondary red, medium grained rock, devoid of quartz, and contained numerous greater and lesser cavities filled by a clear calcite, the individuals of which can occupy several adjacent cavities. In this rock lie lumps or Schlieren of coarse, red pegmatite feldspar (microcline) also enclosed by a coarse network of calcite; in feldspar lumps of this kind one also could find the calcite distributed in the same graphic manner as in the Skarpö occurrence.

The mineral assemblage found together with the calcite in all these rocks is of a characteristic kind. The most conspicuous mineral is an alkali feldspar, grown as borders from the feldspar of the walls of the cavities and protruding as small tables or idiomorphic tops into the calcite (Figs. 5, 6). Crystallographically this border feldspar has the same orientation as the adjacent earlier feldspar, on which it has been formed. In those cases where the earlier feldspar is microcline, the border consists of potassium feldspar, and in the cases when the former is a plagioclase, the border is albite. Idiomorphic alkali feldspar crystals wholly enclosed in the calcite of the cavities and lying free in it can also be seen. The late formed border feldspar is always present

<sup>1</sup> According to R. Looström the lime should have come from without and been deposited secondarily during a superficial partial crushing of the pegmatite, but this is hardly probable. Among other things it does not explain the absence of quartz in the rock.



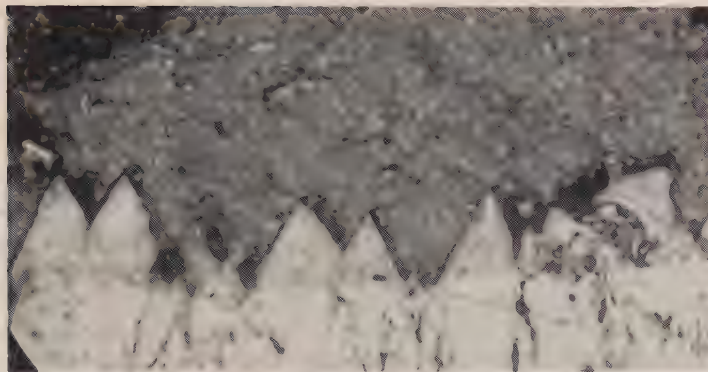


Fig. 5. Border of potassium-feldspar crystals grown on microcline as idiomorphic tops protruding into a calcite filled cavity (the dark substance in the upper part). 220  $\times$ . From Södermalm in Stockholm.

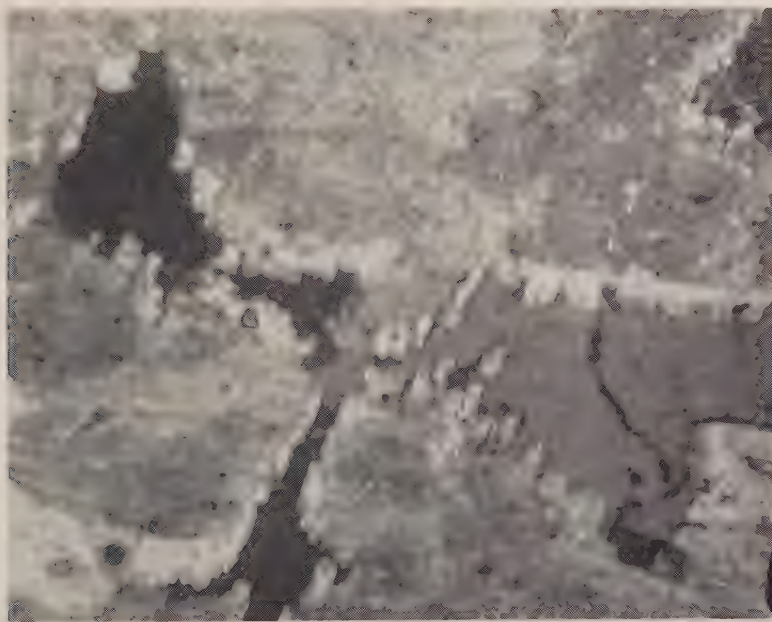


Fig. 6. Small albite tables, forming borders along the walls of cavities in a plagioclase from which the original calcite fillings have been partly dissolved, 45  $\times$ . Skarpö pegmatite mine.

both in the cavities of the graphic feldspar individuals and in the interstices between the feldspar grains in the lime syenite. Other minerals in the lime-filled cavities are some muscovite, chlorite and biotite. Quartz can be found but only in small amounts. In Skarpo the quartz is non-idiomorphic against the feldspar borders but has itself idiomorphic forms against the calcite. In this connection a find by A.

Bygdén may also be mentioned; he found as a rarity on the waste heap specimens consisting of porous agglomerations of small idiomorphic quartz crystals. Probably the cavities in the quartz-aggregates had been filled with calcite together with some alkali-feldspar and micas of which the two latter remained. Thus in the same pegmatite body we have had the nearly quartz-free calcite bearing graphic feldspar rock and mixtures of nearly pure quartz and calcite. Unfortunately it is not known if they have occurred together or not, but the quartz-calcite rock must have been of an inconsiderable quantity.

The feldspar with calcite in a graphic distribution is a peculiar thing. The calcite-filled cavities have strictly the same lamellar forms as the quartz in a graphic feldspar, but the former are filled with two or three generations of minerals, the feldspar borders being oriented parallel to the mother feldspar, the calcite often forming more individuals in one and the same hollow, and the micas and the quartz, if present, being developed as independent grains. It seems inevitable to suppose that the mother feldspar upon its crystallization enclosed a solution that afterwards gave rise to the cavity-filling minerals. If this is correct, the forms of the graphic cavities must have been determined by the feldspar.<sup>1</sup>

A survey of thin sections from loose boulders and in situ finds of lime syenites from different localities of Sweden brings out few new facts. The rocks are generally very salic, and both plagioclase-dominated and potassium-rich rocks are present. The mineral assemblage in the carbonate-filled cavities is similar to that described above. Locally epidote also is seen. In a sample from Vässarö, an island in Upland, prehnite was present in considerable amounts. Fluorite is rarely adjoined.

The quantity of the minerals occupying the cavities is varying. In specimens from Skarpö, A. Bygdén calculated the quantity of quartz—assuming that the substance filling the cavities had been this mineral—to be about 25% on the average (20). The figure may have been raised a little, if the calculation had been made for calcite. In Getlycke the content of the cavities is less, but in the lime syenites the quantity of carbonate can reach 30 to 40%.

The lime syenites have been supposed to obtain their mineralogical properties through assimilation of limestone (21). This is not probable in the three instances studied here, partly because no limestones are known in the surroundings where they occur, and partly because no traces of lime silicates are found in the rocks. Also, the development as small isolated bodies in the interior of a granite or pegmatite, or as a border in the zonally differentiated Getlycke pegmatite, argues against the syntectic theory. According to the view of the writer, the probable interpretation of these peculiar rocks is that they are of magmatic origin, formed through an assembling on a small scale of low melting substances of the kind alluded to in the chapter above on carbonates in a magma. The assembling process may have modified the chemical composition of the granite and pegmatite respectively, and has given rise to the solution from which the minerals were deposited in and between the feldspars. To judge from the filling of the cavities, this solution should have contained mainly calcium carbonate but also the ingredients of the alkali feldspar borders, of some chlorite, muscovite and sometimes biotite and a little quartz. But the solution was a carbonate-rich one, and the potassium, probably before the beginning of crystalliza-

<sup>1</sup> According to A. E. Fersmann (*Z. Krist.* 69, 77, 1929) the parallel orientation of the quartz spindles in graphic feldspar is determined by the growth of the feldspar. The forms of the hieroglyphs on sections perpendicular to the spindles should be the result of an interaction of the crystal form of both minerals.

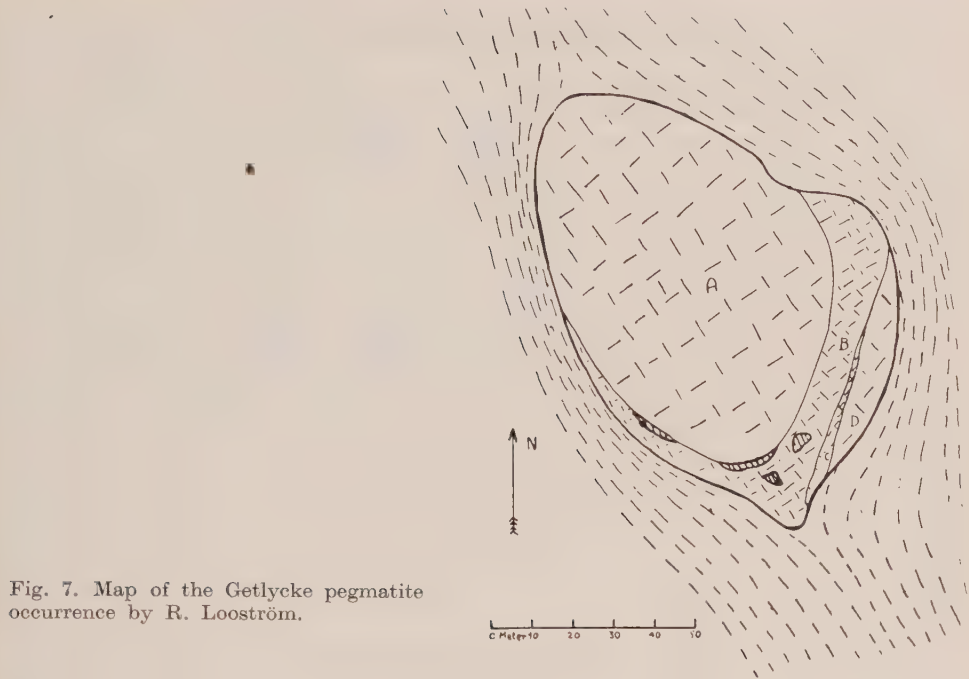


Fig. 7. Map of the Getlycke pegmatite occurrence by R. Looström.

tion, must have been in carbonatic combination and formed double carbonates with  $\text{CaCO}_3$ . Water may also have been present. Indeed the amount of substances assembled in the carbonatite bodies must not have been restricted to that contained in the calcite filled cavities. Originally the amount can have been greater, embracing a greater quantity of potassium as carbonate and hydrate, hydrates of aluminum or aluminates, and possibly also remnants of decomposed (by water and  $\text{CO}_2$ ) potassium and albite feldspar. If substances of this kind are enriched in a small volume of the granite magma the magma will become saturated with them, and they will begin to react with the free  $\text{SiO}_2$  in the granite and tend to give the magma a syenitic character. When crystallization began, the micropertthite and plagioclase were crystallized first, leaving a solution of lower temperature containing the components of the minerals in the cavities. This solution was a carbonatic one, containing double carbonates and  $\text{CaCO}_3$ , and its freezing temperature was low, especially since water had been enriched. At further lowering of the temperature the water may have caused a decomposition of the double carbonates, and the feldspar borders, quartz and micas were formed. The late crystallization of the calcite perhaps is due to the high  $\text{CO}_2$  and  $\text{H}_2\text{O}$  content of the residue and the production of bicarbonate until the surplus of  $\text{CO}_2$  had escaped.

The carbonate-bearing syenite and pegmatite bodies may well be spoken of as carbonatites. According to the theory given above they can be regarded as small embryonic beginnings of alkaline rocks, though the development has in no case as yet known advanced as far as the building of feldspathoides; and a small surplus of  $\text{SiO}_2$  is still present.



### On the genesis of the nepheline syenites

The chief purpose of the present paper is to draw the attention of geologists to the properties of the double carbonates of calcium, magnesium and alkalis and to the role they and mixtures of them and alkali-, calcium- and magnesium-carbonates may play in the production of carbonatites and alkaline rocks. Since it must be regarded as possible that nepheline syenites can be produced both through differentiation in a magma and through assimilation of carbonate rocks, no general conclusion concerning their genesis can be drawn. It must be the task of the investigators in the individual cases to find, if possible, evidence for either of the alternatives.<sup>1</sup> Only in the case of the lime syenites and the calcite-bearing pegmatites that have been studied in some detail has the present author taken a definitive standpoint.

Concerning the Alnö alkaline rocks von Eckermann rejects the possibility of a syntexis of magma and a carbonate rock. The reason for this is partly the absence in the environs of Alnö and in general in this part of Sweden of carbonate rocks in the Archean, but furthermore, according to him the composition of the mother solution makes it impossible to deduce it by syntexis. None of the arguments are conclusive, and, as shown above, a derivation of a magma of this kind by syntexis may theoretically be possible. But the writer joins with him in that it seems to be scarcely probable that the magma should have found a carbonate rock in its way, considering the constitution of the Archean. The same can be said about most of the other occurrences of alkaline rocks in Sweden.

von Eckermann makes no positive statement about the genesis of the Alnö rocks. But if the syntectic origin is rejected, it seems difficult to find any other alternative than that of differentiation from a magma. Also if one thinks of a palingenesis as the origin of the mother liquid, we must deal with magmatic solutions. Perhaps a fact in favour of a magmatic origin of the Alnö mother liquid is its richness in fluorine and also in titanium and phosphorus.

#### ACKNOWLEDGEMENT

The writer is much indebted to Dr. A. Bygdén and Dr. R. Blix for valuable help with melting experiments.

My sincere thanks are also due to the chief of the Mineralogical Department of the State Museum, Prof. F. E. Wickman, for his kindness in placing at my disposal a workplace in the department, where this paper has been prepared.

#### REFERENCES

1. HOLMQUIST, P. J., Bull. geol. Instit. Uppsala *III*, 181, 1897.
2. SUNDIUS, N., Geol. Fören. förhandl. *59*, 246, 1937.
3. NIGGLI, P., Z. anorg. und allg. Chemie *98*, 281, 1916.
4. KRÖGER, C., ILLNER, K. W., and GRAESER, W., Zeitschr. anorg. u. allg. Chemie *251*, 271, 1943.

<sup>1</sup> A good review of the properties of the African carbonatites and of the opinions about the genesis of these peculiar rocks is given in a paper by W. Campbell Smith in Quarterly Journ. Geol. Soc. London, *CXII*, 1956, 189.



5. NIGGLI, P., *Z. anorg. und allg. Chemie* 106, 126, 1919.
6. JAGITSCH, R., JACOBSSON, B., and ROLIN, S., *Proc. Intern. Symposium Reactivity of Solids*, Gothenburg (1952), pt. 2, 771.
7. DE SCHULTEN, A., *Bull. Soc. Fr. Min.* 19, 164, 1896.
8. EITEL, W., and SKALIJS, W., *Zeitschr. anorg. u. allg. Chemie* 183, 272, 1929.
9. LE CHATELIER, *Compt. rend.* 118, 416, 1894.
10. EITEL, W., *Schr. d. Königsberger Gel. Ges., Jahrb.* 1, 164, 1924.
11. DANA, 7th ed., 2, 222.
12. BOWEN, *The evolution of the igneous rocks*, 1928, 234. *Journ. Geol.*, 23, Suppl. 1915, 55.
13. DALY, R. A., *Bull. Golog. Soc. America* 21, 87, 1910, and *Journ. Geol.* XXVI, 97, 1918.
14. BOEKE, *Neues Jahrb. f. Min.* 1, 91, 1912.
15. HÖGBOM, A. G., *Geol. Fören. förhandl.*, Stockholm, 17, 100, 1895.
16. VON ECKERMANN, H., *The alkaline district of Alnö island*, S.G.U., Ser. Ca, No. 36, 1948.
17. VON ECKERMANN, H., *ibid.*, p. 161.
18. HÖGBOM, A. G., *Bull. Geolog. Inst. Upsala* III, 436, 1897.
19. LOOSTRÖM, R., *Geol. Fören. förhandl.* 52, 431, 1930.
20. BYGDÉN, A., *Bull. Inst. Upsala* VII, 16, 1908.
21. BRÖGGER, W. C., *Vidensk.selsk. skrifter*, 1, Mat.-naturv. Klasse, No. 91, 334, 1920.

Tryckt den 4 december 1957

Uppsala 1957. Almqvist & Wiksells Boktryckeri AB



## The chemical composition and symmetry of caryinite

By KURT BOSTRÖM

### ABSTRACT

An X-ray investigation of the original material of Hj. Sjögren (1895) has been made, showing that caryinite is monoclinic, belonging to space group  $P2_1/c$  and having  $a_0 = 11.48 \text{ \AA}$ ,  $b_0 = 13.17 \text{ \AA}$ ,  $c_0 = 6.87 \text{ \AA}$  and  $\beta = 99.0^\circ$ . A new partial chemical analysis shows that caryinite contains  $\text{SiO}_2$ , and by correcting the old analysis, the formula  $(\text{Pb}, \text{Ca}, \text{Na}, \text{Mn})_3(\text{Mg}, \text{Mn})_2(\text{AsO}_4)_3 \cdot y(\text{OH})_x$  is obtained. The unit cell contains 4 formula units.

### Introduction

Caryinite was first described by C. H. Lundström (1874). Unfortunately, his chemical analysis of the mineral was made on impure material. In 1875 A. Sjögren published a paper in which he reported paragenetic observations, stating that caryinite always occurs surrounded by berzeliite. From his observations and the chemical analysis, he drew the conclusion that berzeliite is formed from caryinite. These observations were confirmed by W. Lindgren (1881). In addition Lindgren observed three cleavage planes, all perpendicular to each other. The mineral was therefore regarded as orthorhombic. In the same year, however, Des Cloizeaux made a careful optical investigation of caryinite and noticed that the mineral exhibited horizontal dispersion. He therefore concluded that the symmetry was monoclinic. Hj. Sjögren (1895) made a thorough study of caryinite, but was unable to observe any horizontal dispersion; for this reason and others, he concluded that caryinite must be orthorhombic. Furthermore, he discovered that caryinite is not always surrounded by berzeliite, and it was thus possible for him to have a chemical analysis performed on pure material by R. Mauzelius.

E. Larsen (1921) and N. H. Magnusson (1930) have both studied caryinite, but not from the present point of view.

### Unit cell and space group

The present writer has made an X-ray study of the crystallography of caryinite using the original material of Hj. Sjögren (R.M.A. 221444). The specimen used was about  $0.5 \times 0.1 \times 0.1 \text{ mm}$  in size, and showed cleavage surfaces. Using both unfiltered and Ni-filtered Cu radiation, rotation and Weissenberg equi-inclination photographs (zero, first and second layer lines) were taken, employing the  $c$ -axis as the axis of rotation. Refined values for the unit cell dimensions were obtained from a powder-photograph taken with a Guinier camera.

Table 1. *d*-values for caryinite.

<i>d</i> Å	<i>I</i>	<i>hkl</i>	<i>d</i> Å	<i>I</i>	<i>hkl</i>
8.60	1	110	2.258	1	—
6.50	1	020	2.080	1	152
6.05	1	011	2.072	1	332
5.10	1	—	2.010	1	152
4.54	1	121	1.925	1	442
4.45	1	211	1.900	1	—
4.19	1	121	1.877	1	—
4.09	1	130	1.849	1	532
3.88	1	211	1.841	1	—
3.69	1	031	1.801	1	602?
3.64	1	310	1.748	1	323?
3.39	1	002	1.730	1	—
3.33	1	—	1.714	1	550
3.29	2	040; 112	1.699	1	004
3.21	1	231	1.666	1	—
3.14 <sup>a</sup>	2 <sup>b</sup>	202 <sup>c</sup>	1.641	1	532; 172; 080; 224
3.12	1	321	1.510	1	172
3.03	3	112; 022	1.558	1	471
2.964	1	231	1.551	1	602
2.903	2	112; 141	1.540	1	334
2.868	10	330; 240	1.536	1	—
2.849		400	1.522	1	224; 730
2.810		321	1.507	1	471
2.790	2	—	1.491	1	—
2.730	2	202	1.435	1	570; 372; 381; 642
2.686	5	132; 411; 312	1.414	1	800
2.659	1	—	1.394	1	334
2.536	2	132	1.373	1	105
2.445	1	411	1.360	1	712; 215
2.363	1	042	1.343	1	125
2.329	1	332	1.329	1	105

<sup>a</sup> Calculated.<sup>b</sup> From Weissenberg photograph.<sup>c</sup> Shadowed by first KCl line.The values are as follows ( $\text{Cu } K_{\alpha_1} = 1.5405 \text{ \AA}$ ):

$$a_0 = 11.48 \pm 0.02 \text{ \AA}$$

$$b_0 = 13.17 \pm 0.01 \text{ \AA}$$

$$c_0 = 6.87 \pm 0.01 \text{ \AA}$$

$$\beta = 99.0 \pm 0.1^\circ$$

$$V = 1027 \text{ \AA}^3$$

The *d*-values were determined by means of a Guinier camera ( $\text{Cu } K_{\alpha}$  radiation) using KCl as the standard substance.

In Table 1, the *d*-values are listed.

The reflections observed in the Weissenberg photographs satisfied the following conditions:

$$(hkl) \quad \text{none}$$

$$(h0l) \quad l = 2n$$

$$(0k0) \quad k = 2n$$



These are the conditions stated for space group No. 14 of the International Tables:  $P2_1/c$ . However in addition to these, the following conditions are also satisfied (disregarding a few weak reflections).

$$\begin{aligned}(h k l) \quad h + k + l &= 2n \\ (h 0 l) \quad l &= 2n\end{aligned}$$

The first relationship is satisfied for 183 observed  $(h k 0)$  reflections, and is not satisfied for only 6. It is satisfied for all reflections observed on the first and second layer line photographs. These conditions show that the pseudo-lattice is body-centred, and that a glide plane  $c/2$  is present in it; we therefore have a pseudo space group  $I 2/c$ . This can be transformed into  $I 2/a$  by exchanging the  $a$ - and  $c$ -axes, which is then an alternative setting of space-group No. 15 ( $C 2/c$ ) in the second setting. This space group is a subgroup of No. 230 ( $I a 3 d$ ), the same as that of berzeliite and garnet.

### Chemical composition

The only reliable analysis of caryinite is that performed by Mauzelius and published by Hj. Sjögren (column 1 of Table 2). This analysis is suspicious in that it lacks  $\text{SiO}_2$ , since it has been shown (cf. e.g. Machatschki, 1932) that berzeliite regularly contains small amounts of  $\text{SiO}_2$ . If  $\text{SiO}_2$  is present in the caryinite analysed by Mauzelius, it has almost certainly been included in the  $\text{As}_2\text{O}_5$  value.

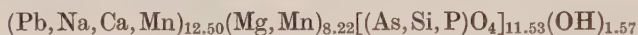
Table 2. The chemical composition of caryinite.

	1	2		3	4	5
$\text{As}_2\text{O}_5$	49.78	49.57	As	11.37	11.53	12
$\text{P}_2\text{O}_5$	0.19	0.19	P	0.07		
$\text{V}_2\text{O}_5$	trace?	—	Si	0.09		
$\text{SiO}_2$	not determined	0.21	Mg	2.02	8.22	8
MgO	3.09	3.09	$\text{Fe}^{2+}$	0.20		
FeO	0.54	0.54	Mn	6.93		
MnO	18.66	18.66	Na	4.39	12.50	12
$\text{Na}_2\text{O}$	5.16	5.16	K	0.21		
$\text{K}_2\text{O}$	0.37	0.37	Ca	5.70		
CaO	12.12	12.12	Ba	0.18		
BaO	1.03	1.03	Pb	1.09		
PbO	9.21	9.21	H	1.57	1.57	—
$\text{H}_2\text{O}$	0.53	0.53	O	47.99	47.99	48
Cl	trace	—				
Total	100.68	100.68		81.81		

1. Original analysis of Mauzelius in Sjögren (1895).
2. Corrected analysis, assuming the  $\text{As}_2\text{O}_5$  value of column 1 to include  $\text{SiO}_2$ .
3. Cell content, assuming structural water. Mol. weight of unit cell = 2654.
4. Number of atoms per unit cell, assuming Mn to distribute itself between the 6 coordinated and the higher coordinated positions as follows: "6" = 6.00 Mn, "higher" = 0.93 Mn.
5. Ideal cell content.

Therefore Dr. R. Blix kindly made a separate  $\text{SiO}_2$  determination on the original material. He found that the  $\text{SiO}_2$  content of this particular caryinite was 0.21 %. The corrected analysis is given in column 2 of Table 2.

It seems plausible that the water content belongs to the structure. The atomic content of the unit cell is given in column 3 of Table 2. The density observed by Mauzelius was  $4.29 \text{ g/cm}^3$  at  $14^\circ\text{C}$ . It also seems natural to assume some correspondence between the formulas of caryinite and berzeliite. Therefore the cations in column 4 of Table 2 have been divided into three groups, one group of cations occurring in oxygen tetrahedra, a second group occurring in octahedra often made up entirely of oxygen atoms, and finally a group of larger cations. Manganese belongs to both of these two latter groups, and has consequently been divided between them, but the major part of it belongs most likely to the group of cations having six-fold coordination. Thus we get the following formula:



Summing up, it seems possible to state the caryinite formula in the following way, the unit cell being regarded as containing 4 of these formula units:  $(\text{Pb, Ca, Na, Mn})_3(\text{Mg, Mn})_2(\text{AsO}_4)_{3-y}(\text{OH})_x$ , where  $x$  and  $y$  are small numbers. It is impossible to say anything about the covariancy of the ions. The removal of  $\text{AsO}_4^{3-}$  creates a small deficit of negative charge, which is balanced by the introduction of  $\text{OH}^-$  ions and by the substitution of univalent cations for bivalent ones. All this shows that it is possible to regard caryinite as a berzeliite containing lead and water, and to suppose that the cause of the non-existence of cubic symmetry resides in the fact that there is a rather large fraction of cations which are larger than calcium.

The hydroxyl content of caryinite can be regarded as similar in nature to that in the garnet group, e.g. the series grossularite-hydrogarnet.

#### ACKNOWLEDGEMENTS

The author wishes to convey his thanks to Prof. F. E. Wickman, Swedish Museum of Natural History, for his kind interest and help, and to Mrs. S. Nord, who took the Guinier photographs.

#### REFERENCES

- DES CLOIZEAUX, M., 1881, Bull. Soc. Min. de France 4, 56.  
 LARSEN, E., 1921, Bull. U.S. Geol. Survey No. 679, 53.  
 LINDGREN, W., 1881, Geol. Fören. Förh. 5, 556.  
 LUNDSTRÖM, C. H., 1874, Geol. Fören. Förh. 2, 178, correction p. 223.  
 MACHATSCHKI, F., 1932, Geol. Fören. Förh. 54, 319.  
 MAGNUSSON, N. H., 1939, Sver. Geol. Unders. Ser. Ca No. 23, pp. 52 and 92.  
 SJÖGREN, A., 1875, Geol. Fören. Förh. 2, 533.  
 SJÖGREN, H. J., 1895, Bull. of the Geol. Inst. of Upsala 2, p. 87.

Tryckt den 4 december 1957

Uppsala 1957. Almqvist & Wiksells Boktryckeri AB

# An attempt to determine the effect of cations on the extinction angle of clinopyroxene $c \wedge \gamma$ with the aid of linear regression equations

By ÅKE HENRIQUES

## SUMMARY

A linear regression equation (No. 2) for the extinction angle  $c \wedge \gamma$  of the clinopyroxene as a function of the mineral's chemical composition has been calculated. The equation is found to be valid only within the limits of chemical variation, in the material studied, and it is thus not allowed to extrapolate its use outside this region.

The investigation was carried out assuming that to the first approximation the extinction angle  $c \wedge \gamma$  varies linearly with the chemical composition. From a quantum-mechanical point of view are, however, small deviations from linear dependence explicable.

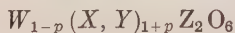
As a basis for the investigation the author has used the determination of optical and chemical properties for clinopyroxenes made by Hess (1949).

The following equation has been used for the extinction angle  $c \wedge \gamma (=u)$ :

$$u = a + \sum a_i N_i \quad (1)$$

where  $a$  is a constant,  $a_i$  represents the effects of cation of type  $i$  on the extinction angle  $u$ .  $N_i$  is the number of the cations in a definite volume.

The general clinopyroxene formula can be written as (Hess, 1949):



where  $W = Ca^{2+}, Na^+, K^+$

$X = Mg^{2+}, Fe^{2+}, Ni^{2+}$

$Y = Al^{3+}, Ti^{4+}, Cr^{3+}, Fe^{3+}$

$Z = Si^{4+}, Al^{3+}, Ti^{4+}, Cr^{3+}, Fe^{3+}$ .

The ideal formula for the clinopyroxene indicates that  $\sum Z$  as well as  $\sum (W + X + Y)$  are both = 2 reckoned on 6 oxygen. According to the electroneutrality  $\sum (lW + lX + lY + lZ) = 12$  where  $l$  is the charge of the different ions. The chemical constituents in the pyroxenes are therefore not all independent variables but inner relationships occur.

Table 1. Calculated and observed extinction angles of the clinopyroxen according to equation (2).

No. <sup>1</sup>	U° calc.	U° obs.	Δ U°	No. <sup>1</sup>	U° calc.	U° obs.	Δ U°
1	39	39	0	20	50	50	0
2	39	40	1	21	43	43	0
3	40	41	1	22	44	46	2
4	42	41	-1	23	45	45	0
5	41	41	0	24	45	44	-1
6	40	41	1	25	48	47	-1
7	42	41	-1	26	45	44	-1
8	41	41	0	27	50	48	-2
9	42	43	1	28	43	44	1
10	42	42	0	29	43	44	1
11	43	42	-1	30	43	44	1
12	44	44	0	31	43	44	1
13	44	43	-1	33	44	44	0
14	46	43	-3	35	39	40	1
15	46	43	-3	36	39	40	1
16	43	43	0	37	45	45	0
17	46	48	2	38	47	48	1
18	47	48	1	39	50	51	1
19	55	57	2				

<sup>1</sup> The same numeration is employed as in Hess' paper.

In calculating the number of cations the Z-positions have been added up with  $\text{Al}^{3+}$  (4) to exactly 2 while the condition  $\Sigma(W + X + Y) = 2$  is not rigorously valid (Table 3). Finally the way in which the number of cations on the basis of 6 oxygen ions have been calculated makes the electroneutrality condition  $\Sigma(lW + lX + lY + lZ)$  exactly fulfilled for all the analyses. Thus two inner relationships exist and in accordance with the theory of regression equations (Hald, 1948) the constant term and  $\text{Al}^{3+}$  (4) are left out.

$$\begin{aligned}
 U = & (-8.86 \pm 7.68) \text{Si}^{4+} + (17.81 \pm 13.29) \text{Al}^{3+} (6) - (18.20 \pm 31.42) \text{Ti}^{4+} - \\
 & - (5.25 \pm 26.40) \text{Cr}^{3+} + (63.88 \pm 10.13) \text{Fe}^{3+} + (39.37 \pm 8.62) \text{Fe}^{2+} + \\
 & + (40.86 \pm 18.17) \text{Mn}^{2+} + (30.75 \pm 8.12) \text{Mg}^{2+} + (24.48 \pm 7.66) \text{Ca}^{2+} + \\
 & + (73.10 \pm 21.93) \text{Na}^{+} - (36.08 \pm 108.25) \text{K}^{+}.
 \end{aligned}
 \tag{2}$$

In spite of fairly good agreement between calculated and observed values on the material from which the regression equations were deduced (Table 1) equation (2) does not seem to represent the variation of the extinction angle with chemical content. The average errors of the regression coefficients are too great (Henriques, 1957). This becomes also apparent with a comparison between values calculated from equation (2) for diopside, hedenbergite, johannsenite, aegirine and jadeite and values given in the literature (Table 2). The main reason for this would seem to be that the contents of a number of ions in the study material were too small (Table 3). In order to reduce the average error of the regression coefficients it is required then that material with a wider variation for all constituent ions be used.



Table 2. Observed and calculated extinction angles of diopside, hedenbergite, johannsenite, aegirine, jadeite according to equation (2).

			U° calc.	U° obs.	U°
Diopside	CaMgSi <sub>2</sub> O <sub>6</sub>	. . . . .	38	38 <sup>1</sup>	0
Hedenbergite	CaFeSi <sub>2</sub> O <sub>6</sub>	. . . . .	46	48 <sup>1</sup>	2
Johannsenite	CaMnSi <sub>2</sub> O <sub>6</sub>	. . . . .	48	48 <sup>2</sup>	0
Aegirine	NaFeSi <sub>2</sub> O <sub>6</sub>	. . . . .	119	98-107 <sup>1</sup>	min. - 12 max. - 21
Jadeite	NaAlSi <sub>3</sub> O <sub>6</sub>	. . . . .	73	33-35 <sup>1</sup>	min. - 38 max. - 40

<sup>1</sup> Tröger (1956)

<sup>2</sup> Schaller (1938)

Table 3.

	Ranges of the proportions of cations on the basis of six oxygen atoms		Average error in regression coefficients in equation 2
	min.	max.	
Si <sup>4+</sup> . . . . .	1.751	1.988	7.68
Al <sup>3+</sup> (6) . . . . .	0.001	0.104	13.29
Ti <sup>4+</sup> . . . . .	0.001	0.043	31.42
Cr <sup>3+</sup> . . . . .	0.000	0.035	26.40
Fe <sup>3+</sup> . . . . .	0.009	0.173	10.13
Fe <sup>2+</sup> . . . . .	0.028	0.925	8.62
Mn <sup>2+</sup> . . . . .	0.002	0.129	18.17
Mg <sup>2+</sup> . . . . .	0.019	1.064	8.12
Ca <sup>2+</sup> . . . . .	0.703	0.972	7.66
Na <sup>+</sup> . . . . .	0.004	0.120	21.93
K <sup>+</sup> . . . . .	0.000	0.008	108.25

The regression equation was solved with a digital computer (BESK) by the method of squares in accordance with the Gauss elimination method. The average error was calculated in accordance with the formula:

$$\left( X_{i,i+2} \cdot \frac{V^2}{m-n} \right)^{1/2}$$

where  $X_{i,i+2}$  is the diagonal element belonging to  $X_i$  in the diagonal element of the inverse matrix. It is finally mentioned that no account was taken of errors in the physical and chemical determinations in the derivation of the regression equations.

#### ACKNOWLEDGEMENT

The author wishes to convey his thanks to Prof. F. E. Wickman for his critical reading of the manuscript.

REFERENCES

- HALD, A. (1948), Statistiske metoder. København.  
HENRIQUES, Å. (1958), The influence of cations on the optical properties of clinopyroxenes.  
Part. I., Arkiv för Mineralogi och Geologi, 2, no. 24.  
HESS, H. H. (1949), Chemical composition and optical properties of common clinopyroxenes.  
Part. I., Am. Min., 34, 621-666.  
SCHALLER, W. T. (1938), Johannsenite, A new manganese pyroxene. Am. Min., 23, 575-582.  
TRÖGER, W. E. (1956), Optische Bestimmung der gesteinsbildenden Minerale. Teil 1, Bestimmungstabellen. Stuttgart.

Tryckt den 24 februari 1958

Uppsala 1958. Almqvist & Wiksells Boktryckeri AB

# The influence of cations on the optical properties of clinopyroxenes

## Part I

By ÅKE HENRIQUES

### SUMMARY

Regression equations for the optical properties ( $\alpha$ ,  $\beta$ ,  $\gamma$  and  $2V$ ) as a function of the chemical composition of clinopyroxene have been calculated. Comparisons with earlier investigations of the same type are made.

### Introduction

Hori (1954 and 1956) studied the optical properties of pyroxene as a function of the chemical composition. He took as an approximation that the optical properties for phases with similar crystal structures vary linearly with the chemical composition. He indicated, however, that from a quantum-mechanical point of view deviations from linear dependence are explicable. A treatment of the problem with regard to this subject would, however, be extremely complicated. For  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $2V$  Hori postulated equations of the type:

$$\alpha = a_{\alpha} + \sum a_{i\alpha} N_i \quad (1)$$

$$\beta = a_{\beta} + \sum a_{i\beta} N_i \quad (2)$$

$$\gamma = a_{\gamma} + \sum a_{i\gamma} N_i \quad (3)$$

$$2V = a_{2V} + \sum a_{i2V} N_i \quad (4)$$

where  $a_{\alpha}$ ,  $a_{\beta}$ ,  $a_{\gamma}$  and  $a_{2V}$  are constants,  $a_{i\alpha}$ ,  $a_{i\beta}$ ,  $a_{i\gamma}$  and  $a_{i2V}$  represent the effects of the cation of type  $i$  on the refractive indices  $\alpha$ ,  $\beta$ ,  $\gamma$  and the optic axial angle  $2V$ .  $N_i$  is the number of the cations in a definite volume. As a basis for the investigation Hori employed determinations of optical and chemical properties of clinopyroxenes made by Hess (1949). On the same material the author has worked out anew the corresponding regression equations. Moreover the average error of the regression coefficients as well as the changes in the optical properties during ionic substitution have been determined. Comparison between the author's and Hori's values of corresponding regression coefficients does not show good agreement. This is due to the incorrect mathematical form of Hori's regression equations. (See below.)

Table 1. Calculated and observed refractive indices of clinopyroxenes according to equations (5-7).

No.	$\alpha_{\text{calc.}}$	$\alpha_{\text{obs.}}$	$\Delta \alpha$	$\beta_{\text{calc.}}$	$\beta_{\text{obs.}}$	$\Delta \beta$	$\gamma_{\text{calc.}}$	$\gamma_{\text{obs.}}$	$\Delta \gamma$
1	1.672	1.672	0.000	1.680	1.678	-0.002	1.702	1.701	-0.001
2	1.675	1.674	-0.001	1.681	1.680	-0.001	1.702	1.702	0.000
3	1.678	1.680	0.002	1.683	1.685	0.002	1.705	1.706	0.001
4	1.681	1.681	0.000	1.686	1.685	-0.001	1.708	1.706	-0.002
5	1.680	1.681	0.001	1.685	1.685	0.000	1.706	1.708	0.002
6	1.681	1.682	0.001	1.686	1.687	0.001	1.708	1.709	0.001
7	1.685	1.683	-0.002	1.690	1.686	-0.004	1.712	1.709	-0.003
8	1.681	1.682	0.001	1.686	1.687	0.001	1.709	1.709	0.000
9	1.683	1.682	-0.001	1.688	1.688	0.000	1.711	1.710	-0.001
10	1.684	1.683	-0.001	1.689	1.687	-0.002	1.711	1.710	-0.001
11	1.688	1.687	-0.001	1.693	1.692	-0.001	1.716	1.715	-0.001
12	1.692	1.691	-0.001	1.697	1.695	-0.002	1.720	1.719	-0.001
13	1.693	1.692	-0.001	1.699	1.697	-0.002	1.721	1.719	-0.002
14	1.699	1.699	0.000	1.706	1.706	0.000	1.727	1.727	0.000
15	1.699	1.700	0.001	1.707	1.706	-0.001	1.728	1.728	0.000
16	1.706	1.708	0.002	1.713	1.714	0.001	1.734	1.736	0.002
17	1.707	1.708	0.001	1.713	1.715	0.002	1.735	1.735	0.000
18	1.723	1.723	0.000	1.730	1.730	0.000	1.751	1.751	0.000
19	1.735	1.736	0.001	1.743	1.745	0.002	1.764	1.765	0.001
20	1.696	1.698	0.002	1.704	1.706	0.002	1.724	1.724	0.000
21	1.692	1.689	-0.003	1.698	1.695	-0.003	1.719	1.716	-0.003
22	1.694	1.693	-0.001	1.700	1.698	-0.002	1.721	1.720	-0.001
23	1.704	1.699	-0.005	1.710	1.705	-0.005	1.730	1.726	-0.004
24	1.708	1.709	0.001	1.713	1.714	0.001	1.733	1.734	0.001
25	1.713	1.715	0.002	1.718	1.721	0.003	1.738	1.740	0.002
26	1.712	1.710	-0.002	1.718	1.715	-0.003	1.739	1.735	-0.004
27	1.729	1.726	-0.003	1.736	1.733	-0.003	1.758	1.755	-0.003
28	1.691	1.693	0.002	1.695	1.697	0.002	1.719	1.722	0.003
29	1.693	1.694	0.001	1.698	1.698	0.000	1.721	1.722	0.001
30	1.692	1.694	0.002	1.697	1.698	0.001	1.720	1.722	0.002
31	1.694	1.695	0.001	1.698	1.701	0.003	1.722	1.725	0.003
33	1.696	1.697	0.001	1.700	1.701	0.001	1.725	1.724	-0.001
35	1.671	1.672	0.001	1.677	1.679	0.002	1.700	1.701	0.001
36	1.672	1.674	0.002	1.679	1.681	0.002	1.701	1.703	0.002
37	1.696	1.692	-0.004	1.703	1.698	-0.005	1.723	1.719	-0.004
38	1.706	1.707	0.001	1.713	1.714	0.001	1.732	1.733	0.001
39	1.719	1.721	0.002	1.727	1.729	0.002	1.744	1.746	0.002

The general formula for clinopyroxenes may be written (Hess, 1949):

$$W_{1-p}(X, Y)_{1+p}Z_2O_6$$

where  $W = \text{Ca}^{2+}, \text{Na}^+, \text{K}^+$

$X = \text{Mg}^{2+}, \text{Fe}^{2+}, \text{Mn}^{2+}, \text{Ni}^{2+}$

$Y = \text{Al}^{3+}, \text{Ti}^{4+}, \text{Cr}^{3+}, \text{Fe}^{3+}$

$Z = \text{Si}^{4+}, \text{Al}^{3+}, \text{Ti}^{4+}, \text{Cr}^{3+}, \text{Fe}^{3+}.$

If  $\text{Si}^{4+}$  is less than 2 then  $\text{Al}^{3+}, \text{Ti}^{4+}, \text{Cr}^{3+}$  or  $\text{Fe}^{3+}$  will take a corresponding position (with tetrahedral coordination). For the pyroxenes from which the regression equa-



Table 2. Calculated and observed optical angles of clinopyroxenes according to equation (8).

No.	2 $V_{\text{calc.}}$	2 $V_{\text{obs.}}$	$\Delta 2 V$	No.	2 $V_{\text{calc.}}$	2 $V_{\text{obs.}}$	$\Delta 2 V$
1	57	58	1	20	66	66	0
2	53	56	3	21	53	56	3
3	50	50	0	22	56	55	-1
4	48	49	1	23	56	56	0
5	50	49	-1	24	55	56	1
6	50	49	-1	25	58	57	-1
7	49	48	-1	26	54	54	0
8	50	52	2	27	60	59	-1
9	50	52	2	28	46	44	-2
10	48	52	4	29	47	47	0
11	48	51	3	30	46	47	1
12	48	48	0	31	46	49	3
13	54	51	-3	33	44	40	-4
14	59	58	-1	35	56	57	1
15	59	49	-10	36	56	57	1
16	60	60	0	37	61	59	-2
17	56	57	1	38	63	62	-1
18	61	63	2	39	65	68	3
19	66	70	4				

tions were worked out  $\text{Ti}^{4+}$ ,  $\text{Cr}^{3+}$  or  $\text{Fe}^{3+}$  did not need to be used. The aluminium content was in all cases sufficient.

The formula of the clinopyroxene indicates that  $\Sigma Z$  and  $\Sigma(W + X + Y)$  are both = 2 reckoned on 6 oxygen. According to the electroneutrality  $\Sigma(lW + lX + lY + lZ)$  is = 12 where  $l$  is the charge of the different ions. The chemical constituents of the pyroxene are therefore not all independent variables but three inner relationships occur.

In calculating the number of cations the Z-positions have been added up with  $\text{Al}^{3+}$  (4) to exactly 2 while the condition  $\Sigma(W + X + Y) = 2$  is not rigorously valid. Finally the way in which the number of cations on the basis of 6 oxygen ions have been calculated makes the electroneutrality condition  $\Sigma(lW + lX + lY + lZ)$  exactly fulfilled for all the analyses. Thus two inner relationships exist. In order to permit solution of the equation systems (1-4) the constant and one of the ion types must be removed. It is certainly possible to obtain solutions containing both constants and all ionic varieties but on account of the above reasons such equations cannot be ascribed any real importance (Hald, 1948). (Hori, however, neglected this in the solution of the regression equations.)

Optical properties for clinopyroxenes according to equations of the type (1-4).

$$\begin{aligned} \alpha = & (0.231 \pm 0.013) \text{ Si} + (0.868 \pm 0.022) \text{ Al (6)} + (1.190 \pm 0.052) \text{ Ti} + \\ & (0.960 \pm 0.043) \text{ Cr} + (0.970 \pm 0.017) \text{ Fe}^{3+} + (0.657 \pm 0.014) \text{ Fe}^{2+} + \\ & (0.614 \pm 0.030) \text{ Mn} + (0.592 \pm 0.013) \text{ Mg} + (0.611 \pm 0.013) \text{ Ca} + \\ & (0.348 \pm 0.036) \text{ Na} + (0.050 \pm 0.178) \text{ K.} \end{aligned} \quad (5)$$

Table 3. Calculated and observed refractive indices of clinopyroxenes according to equations (11–13).

No.	$\alpha_{\text{calc.}}$	$\alpha_{\text{obs.}}$	$\Delta \alpha$	$\beta_{\text{calc.}}$	$\beta_{\text{obs.}}$	$\Delta \beta$	$\gamma_{\text{calc.}}$	$\gamma_{\text{obs.}}$	$\Delta \gamma$
1	1.673	1.672	-0.001	1.679	1.678	-0.001	1.701	1.701	0.000
2	1.675	1.674	-0.001	1.680	1.680	0.000	1.701	1.702	0.001
3	1.679	1.680	0.001	1.683	1.684	0.001	1.704	1.706	0.002
4	1.682	1.681	-0.001	1.686	1.685	-0.001	1.707	1.706	-0.001
5	1.680	1.681	0.001	1.684	1.685	0.001	1.705	1.708	0.003
6	1.682	1.682	0.000	1.685	1.687	0.002	1.707	1.709	0.002
7	1.686	1.683	-0.003	1.689	1.686	-0.003	1.711	1.709	-0.002
8	1.681	1.682	0.001	1.685	1.687	0.002	1.707	1.709	0.002
9	1.684	1.682	-0.002	1.688	1.688	0.000	1.710	1.710	0.000
10	1.684	1.683	-0.001	1.688	1.687	-0.001	1.710	1.710	0.000
11	1.689	1.687	-0.002	1.692	1.692	0.000	1.715	1.715	0.000
12	1.692	1.691	-0.001	1.696	1.695	-0.001	1.719	1.719	0.000
13	1.694	1.692	-0.002	1.698	1.697	-0.001	1.719	1.719	0.000
14	1.700	1.699	-0.001	1.705	1.706	0.001	1.726	1.727	0.001
15	1.700	1.700	0.000	1.706	1.706	0.000	1.726	1.728	0.002
16	1.706	1.708	0.002	1.712	1.714	0.002	1.734	1.736	0.002
17	1.708	1.708	0.000	1.713	1.715	0.002	1.734	1.735	0.001
18	1.723	1.723	0.000	1.729	1.730	0.001	1.750	1.751	0.001
19	1.736	1.736	0.000	1.744	1.745	0.001	1.763	1.765	0.002
20	1.696	1.698	0.002	1.703	1.706	0.003	1.722	1.724	0.002
21	1.692	1.689	-0.003	1.697	1.695	-0.002	1.718	1.716	-0.002
22	1.694	1.693	-0.001	1.699	1.698	-0.001	1.720	1.720	0.000
23	1.704	1.699	-0.005	1.709	1.705	-0.004	1.729	1.726	-0.003
24	1.707	1.709	0.002	1.712	1.714	0.002	1.731	1.734	0.003
25	1.713	1.715	0.002	1.718	1.721	0.003	1.737	1.740	0.003
26	1.712	1.710	-0.002	1.717	1.715	-0.002	1.738	1.735	-0.003
27	1.728	1.726	-0.002	1.734	1.733	-0.001	1.756	1.755	-0.001
28	1.692	1.693	0.001	1.695	1.697	0.002	1.718	1.722	0.004
29	1.694	1.694	0.000	1.697	1.698	0.001	1.720	1.722	0.002
30	1.693	1.694	0.001	1.696	1.698	0.002	1.719	1.722	0.003
31	1.692	1.695	0.003	1.698	1.701	0.003	1.721	1.725	0.004
33	1.693	1.697	0.004	1.700	1.701	0.001	1.724	1.724	0.000
35	1.672	1.672	0.000	1.677	1.679	0.002	1.700	1.701	0.001
36	1.673	1.674	0.001	1.678	1.681	0.003	1.700	1.703	0.003
37	1.696	1.692	-0.004	1.702	1.698	-0.004	1.722	1.719	-0.003
38	1.706	1.707	0.001	1.712	1.714	0.002	1.731	1.733	0.002
39	1.720	1.721	0.001	1.726	1.729	0.003	1.743	1.746	0.003

$$\begin{aligned} \beta = & (0.239 \pm 0.013) \text{ Si} + (0.855 \pm 0.023) \text{ Al (6)} + (1.164 \pm 0.054) \text{ Ti} + \\ & (0.962 \pm 0.045) \text{ Cr} + (0.979 \pm 0.017) \text{ Fe}^{3+} + (0.649 \pm 0.015) \text{ Fe}^{2+} + \\ & (0.605 \pm 0.031) \text{ Mn} + (0.584 \pm 0.014) \text{ Mg} + (0.610 \pm 0.013) \text{ Ca} + \\ & (0.352 \pm 0.038) \text{ Na} + (0.070 \pm 0.186) \text{ K}. \end{aligned} \quad (6)$$

$$\begin{aligned} \gamma = & (0.253 \pm 0.013) \text{ Si} + (0.847 \pm 0.023) \text{ Al (6)} + (1.232 \pm 0.054) \text{ Ti} + \\ & (0.929 \pm 0.045) \text{ Cr} + (0.964 \pm 0.017) \text{ Fe}^{3+} + (0.649 \pm 0.015) \text{ Fe}^{2+} + \\ & (0.596 \pm 0.031) \text{ Mn} + (0.585 \pm 0.014) \text{ Mg} + (0.604 \pm 0.013) \text{ Ca} + \\ & (0.334 \pm 0.037) \text{ Na} + (0.169 \pm 0.184) \text{ K}. \end{aligned} \quad (7)$$

Table 4. Calculated and observed optical angles of clinopyroxenes according to equation (14).

No.	$2 V_{\text{calc.}}$	$2 V_{\text{obs.}}$	$\nabla 2 V$	No.	$2 V_{\text{calc.}}$	$2 V_{\text{obs.}}$	$\Delta 2 V$
1	57	58	1	20	66	66	0
2	53	56	3	21	53	56	3
3	51	50	-1	22	56	55	-1
4	48	49	1	23	56	56	0
5	50	49	-1	24	55	56	1
6	50	49	-1	25	59	57	-2
7	49	48	-1	26	54	54	0
8	50	52	2	27	60	59	-1
9	50	52	2	28	46	44	-2
10	48	52	4	29	47	47	0
11	48	51	3	30	46	47	1
12	48	48	0	31	46	49	3
13	54	51	-3	33	44	40	-4
14	59	58	-1	35	56	57	1
15	59	49	-10	36	56	57	1
16	60	60	0	37	61	59	-2
16	56	57	1	38	63	62	-1
18	61	63	2	39	66	68	2
19	66	70	4				

$$2 V = (2.98 \pm 17.07) \text{ Si} + (7.90 \pm 29.53) \text{ Al (6)} - (177.37 \pm 69.83) \text{ Ti} + (55.60 \pm 58.68) \text{ Cr} + (59.03 \pm 22.52) \text{ Fe}^{3+} + (11.39 \pm 19.16) \text{ Fe}^{2+} + (1.84 \pm 40.38) \text{ Mn} + (4.29 \pm 18.04) \text{ Mg} + (45.01 \pm 17.01) \text{ Ca} + (84.60 \pm 48.74) \text{ Na} + (124.09 \pm 240.61) \text{ K.} \quad (8)$$

$$\alpha = (0.823 \pm 0.002) \text{ Si} + (0.884 \pm 0.018) \text{ Al (4)} - (0.036 \pm 0.020) \text{ Al (6)} + (0.031 \pm 0.065) \text{ Ti} + (0.090 \pm 0.047) \text{ Cr} + (0.089 \pm 0.243) \text{ Fe}^{3+} + (0.066 \pm 0.003) \text{ Fe}^{2+} + (0.006 \pm 0.023) \text{ Mn} + (0.019 \pm 0.005) \text{ Ca} + (0.031 \pm 0.029) \text{ Na} + (0.050 \pm 0.161) \text{ K.} \quad (9)$$

$$\beta = (0.823 \pm 0.002) \text{ Si} + (0.872 \pm 0.018) \text{ Al (4)} - (0.036 \pm 0.020) \text{ Al (6)} + (0.021 \pm 0.067) \text{ Ti} + (0.104 \pm 0.049) \text{ Cr} + (0.110 \pm 0.025) \text{ Fe}^{3+} + (0.068 \pm 0.003) \text{ Fe}^{2+} + (0.006 \pm 0.023) \text{ Mn} + (0.026 \pm 0.006) \text{ Ca} + (0.040 \pm 0.029) \text{ Na} + (0.069 \pm 0.165) \text{ K.} \quad (10)$$

$$\alpha = (0.519 \pm 0.011) \text{ Si} + (0.429 \pm 0.010) \text{ Al} + (0.626 \pm 0.058) \text{ Ti} + (0.537 \pm 0.043) \text{ Cr} + (0.542 \pm 0.018) \text{ Fe}^{3+} + (0.370 \pm 0.012) \text{ Fe}^{2+} + (0.319 \pm 0.026) \text{ Mn} + (0.305 \pm 0.011) \text{ Mg} + (0.323 \pm 0.011) \text{ Ca} + (0.194 \pm 0.034) \text{ Na} + (0.049 \pm 0.167) \text{ K.} \quad (11)$$

Table 5. Changes in the refractive indices of clinopyroxenes v

		Substituting			
		Al	Ti	Cr	Fe <sup>3+</sup>
Si	$\delta \alpha \times 10^3$	$-0.90 \pm 0.15$			
	$\delta \beta \times 10^3$	$-0.99 \pm 0.15$			
	$\delta \gamma \times 10^3$	$-1.14 \pm 0.15$			
	$\delta 2 V \times 10^2$	$-1.38 \pm 21.20$			
Ca	$\delta \alpha \times 10^3$	$+1.06 \pm 0.15$	$+3.03 \pm 0.59$	$+2.14 \pm 0.44$	$+2.19 \pm 0$
	$\delta \beta \times 10^3$	$+0.97 \pm 0.16$	$+2.82 \pm 0.61$	$+2.19 \pm 0.47$	$+2.32 \pm 0$
	$\delta \gamma \times 10^3$	$+0.95 \pm 0.16$	$+3.58 \pm 0.60$	$+1.93 \pm 0.47$	$+2.22 \pm 0$
	$\delta 2 V \times 10^2$	$-38.03 \pm 21.95$	$-226.38 \pm 84.80$	$+8.88 \pm 16.59$	$+12.52 \pm 30$
Mg	$\delta \alpha \times 10^3$	$+1.24 \pm 0.15$	$+3.21 \pm 0.59$	$+2.32 \pm 0.45$	$+2.37 \pm 0$
	$\delta \beta \times 10^3$	$+1.22 \pm 0.15$	$+3.07 \pm 0.61$	$+2.44 \pm 0.46$	$+2.57 \pm 0$
	$\delta \gamma \times 10^3$	$+1.15 \pm 0.15$	$+3.78 \pm 0.60$	$+2.13 \pm 0.46$	$+2.42 \pm 0$
	$\delta 2 V \times 10^2$	$+2.62 \pm 21.55$	$-185.73 \pm 84.70$	$+49.53 \pm 16.05$	$+53.17 \pm 30$
Fe <sup>2+</sup>	$\delta \alpha \times 10^3$	$+0.59 \pm 0.16$	$+2.56 \pm 0.59$	$+1.67 \pm 0.45$	$+1.72 \pm 0$
	$\delta \beta \times 10^3$	$+0.56 \pm 0.16$	$+2.41 \pm 0.61$	$+1.78 \pm 0.47$	$+1.91 \pm 0$
	$\delta \gamma \times 10^3$	$+0.50 \pm 0.16$	$+3.13 \pm 0.60$	$+1.48 \pm 0.47$	$+1.77 \pm 0$
	$\delta 2 V \times 10^2$	$-4.51 \pm 22.15$	$-192.86 \pm 84.80$	$+42.40 \pm 16.85$	$+46.04 \pm 30$

$$\begin{aligned} \beta = & (0.522 \pm 0.011) \text{ Si} + (0.423 \pm 0.010) \text{ Al} + (0.608 \pm 0.060) \text{ Ti} + \\ & (0.545 \pm 0.045) \text{ Cr} + (0.558 \pm 0.018) \text{ Fe}^{3+} + (0.367 \pm 0.012) \text{ Fe}^{2+} + \\ & (0.314 \pm 0.027) \text{ Mn} + (0.301 \pm 0.011) \text{ Mg} + (0.326 \pm 0.012) \text{ Ca} + \\ & (0.201 \pm 0.035) \text{ Na} + (0.069 \pm 0.173) \text{ K}. \end{aligned} \quad (12)$$

$$\begin{aligned} \gamma = & (0.533 \pm 0.011) \text{ Si} + (0.419 \pm 0.010) \text{ Al} + (0.682 \pm 0.059) \text{ Ti} + \\ & (0.517 \pm 0.045) \text{ Cr} + (0.546 \pm 0.018) \text{ Fe}^{3+} + (0.369 \pm 0.012) \text{ Fe}^{2+} + \\ & (0.308 \pm 0.027) \text{ Mn} + (0.304 \pm 0.011) \text{ Mg} + (0.324 \pm 0.012) \text{ Ca} + \\ & (0.184 \pm 0.035) \text{ Na} + (0.168 \pm 0.172) \text{ K}. \end{aligned} \quad (13)$$

$$\begin{aligned} 2 V = & (5.65 \pm 15.37) \text{ Si} + (4.27 \pm 14.59) \text{ Al} - (184.08 \pm 83.17) \text{ Ti} + \\ & (51.18 \pm 2.36) \text{ Cr} + (54.82 \pm 25.70) \text{ Fe}^{3+} + (8.78 \pm 16.68) \text{ Fe}^{2+} - \\ & (0.75 \pm 38.17) \text{ Mn} + (1.65 \pm 15.86) \text{ Mg} + (42.30 \pm 16.42) \text{ Ca} + \\ & (83.15 \pm 48.65) \text{ Na} + (123.34 \pm 240.55) \text{ K}. \end{aligned} \quad (14)$$

Three different solutions of the equation system were made where the constant and Al<sup>3+</sup> (4) were left out (5–8). Also the constant and magnesium were left out (9–10) and finally the constant was left out while Al<sup>3+</sup> (6) and Al<sup>3+</sup> (4) were combined (11–14).

From the equations it is seen that the linear connexion between optical properties



a substitutions by 1 per cent according to the equations (11–13).

Si, Ca, Mg or Fe <sup>2+</sup>				
Fe <sup>2+</sup>	Mn	Mg	Ca	Na
+ 0.47 ± 0.16	– 0.04 ± 0.28	– 0.18 ± 0.16	—	– 1.29 ± 0.36
+ 0.41 ± 0.17	– 0.12 ± 0.30	– 0.25 ± 0.16	—	– 1.25 ± 0.37
+ 0.45 ± 0.17	– 0.16 ± 0.30	– 0.20 ± 0.16	—	– 1.40 ± 0.37
– 33.52 ± 23.40	– 43.05 ± 41.50	– 40.65 ± 22.85	—	+ 40.85 ± 51.40
+ 0.65 ± 0.16	+ 0.14 ± 0.28	—	+ 0.18 ± 0.16	– 1.11 ± 0.36
+ 0.66 ± 0.16	+ 0.13 ± 0.29	—	+ 0.25 ± 0.16	– 1.00 ± 0.37
+ 0.65 ± 0.16	+ 0.04 ± 0.29	—	+ 0.20 ± 0.16	– 1.20 ± 0.37
+ 7.13 ± 23.00	– 2.40 ± 41.30	—	+ 40.65 ± 22.85	+ 81.50 ± 51.20
—	– 0.51 ± 0.29	– 0.65 ± 0.16	– 0.47 ± 0.16	– 1.76 ± 0.36
—	– 0.53 ± 0.30	– 0.66 ± 0.16	– 0.41 ± 0.17	– 1.66 ± 0.37
—	– 0.61 ± 0.30	– 0.65 ± 0.16	– 0.45 ± 0.17	– 1.85 ± 0.37
—	– 9.53 ± 41.65	– 7.13 ± 23.00	+ 33.52 ± 23.40	+ 74.37 ± 51.45

and chemical content assumed by Hori seems to agree well for  $\alpha$ ,  $\beta$  and  $\gamma$  for which the regression coefficients average error is small, compared with the coefficients (with the exception of  $K^+$ , which is explained by the small, little-varying  $K$ -contents in the material analyzed). This is not so for  $2V$ . Only certain ionic types have an obvious correlation which means that these equations cannot be said to represent the variation of the axial angle with the contents in spite of the fairly good agreement of the material investigated given by them between calculated and observed values. This becomes clear from Tables 2 and 4. It is here pointed out that good agreement between observed and calculated values on the material from which the regression equations were derived is not criterium of the validity of the equations in general cases. The average errors of the regression coefficients must also be small.

Compared with Hori's equations it is obvious how in the new equations each ionic type gives an almost equal increase to  $\alpha$ ,  $\beta$  and  $\gamma$ .

In Tables (1–4) calculated and determined values for refraction and optic axial angle are presented.

The above solutions of the regression equations as well as the great number of such possibilities gives each a regression coefficient for each ionic variety which is usually not identical for the different equations on account of the approximations made for mathematical reasons. It is therefore not possible to exactly determine the change in the optical properties caused by ionic substitution. In Table 5, however, the dimension and the average error of the change in the optical properties in substitution have been calculated for the solution of the regression equations in which the constant has been eliminated and  $Al^{3+}$  (6) and  $Al^{3+}$  (4) combined.

The regression equations were solved with a digital computer (BESK) by the

method of squares in accordance with the Gauss elimination method. The average error was calculated in accordance with the formula:

$$\left( X_{i, i+2} \cdot \frac{V^2}{m-n} \right)^{\frac{1}{2}}$$

where  $X_{i, i+2}$  is the diagonal element belonging to  $X_i$  in the diagonal element of the inverse matrix. It is finally mentioned that no account was taken of errors in the physical and chemical determinations in the derivation of the regression equations.

#### ACKNOWLEDGEMENTS

The author wishes to convey his thanks to Prof. F. E. Wickman, for his critical reading of the manuscript, to Dr. K. Arle and Mr. L. Jansson for mathematical collaboration.

#### REFERENCES

- HALD, A. (1948), *Statistiske metoder*. København.  
HESS, H. H. (1949), Chemical composition and optical properties of common clinopyroxenes. Part I., *Am. Min.*, **34**, 621–666.  
HORI, F. (1954), Effects of Constituents Cations on the Optical Properties of Clinopyroxenes. Scientific Papers of the College of General Education University of Tokyo, *IV*, 71–83.  
— (1956), Effects of Constituent Cations on the Refractive Indices of Orthopyroxenes. *Mineralogical Journal*. Vol. 1, No. 6, 359–371 (Tokyo).

Tryckt den 24 februari 1958

Uppsala 1958. Almqvist & Wiksells Boktryckeri AB

## On the determination of the composition of garnet without chemical analyses

By ÅKE HENRIQUES

In connexion with a study of the manganese rich skarn association of Central Sweden iron ores, it was found necessary to determine the rough chemical compositions of a number of garnets, as far as possible, without chemical analyses. Regression equations for the chemical composition of garnet as a function of the unit cell length and refraction of the mineral were therefore deduced. In the working out of the equations the author assumed that both the unit cell length and the refraction vary linearly with the chemical composition. It seems, however, possible that small deviations from the linear may occur within the garnet group. Material for the investigation was taken from a paper by Frietsch (1957).

The regression equations (Table 1) show that the average error of the respective regression coefficients is far too great to permit an approximative determination of the composition of the garnet. The author has also attempted to determine the chemical composition of the garnet using the same material where even the density (calculated) and the spessartite content is known (Table 2). It is, however, apparent that even in this case the average error of the regression coefficients is too great to permit determination of the composition of the garnet. This becomes also apparent by comparing the observed values and the calculated values of the chemical composition of the garnet from the equations from which the regression equations were worked out (Tables 3 and 4). Sometimes good agreement is obtained between calculated and determined values (see nos. 4 and 26), while in other cases quite different results are obtained (see nos. 9 and 19). The reason is chiefly that it is mathema-

*Table 1.* Regression equation for the chemical composition of the garnet as a function of the unit cell length and the refraction of the mineral.

$\text{Gr} = [3.69 \pm 1.92 + (0.86 \pm 0.13) a_0 - (7.49 \pm 0.79) n] \cdot 100$
$\text{An} = [-23.84 \pm 1.40 + (1.42 \pm 0.09) a_0 + (4.09 \pm 0.58) n] \cdot 100$
$\text{Al} = [15.69 \pm 3.19 - (1.56 \pm 0.21) a_0 + (1.60 \pm 1.31) n] \cdot 100$
$\text{Sp} = [2.69 \pm 5.04 - (0.56 \pm 0.33) a_0 + (2.21 \pm 2.08) n] \cdot 100$
$\text{Py} = [1 - \text{Gr} - \text{An} - \text{Al} - \text{Sp}] \cdot 100$

Table 2. Regression equations for the chemical composition of the garnet as a function of the unit cell length, refraction, density and content of spessartite.

$\text{Gr} = [12.22 \pm 5.67 - (0.05 \pm 0.56) \alpha_0 - (4.44 \pm 1.95) n - (0.83 \pm 0.55) D - (0.01 \pm 0.12) \text{Sp}] \cdot 100$
$\text{An} = [-30.40 \pm 3.86 + (2.06 \pm 0.38) \alpha_0 + (2.06 \pm 1.33) n + (0.70 \pm 0.37) D - (0.24 \pm 0.08) \text{Sp}] \cdot 100$
$\text{Al} = [10.34 \pm 4.33 - (1.17 \pm 0.43) \alpha_0 + (0.56 \pm 1.49) n + (0.70 \pm 0.42) D - (0.68 \pm 0.09) \text{Sp}] \cdot 100$
$\text{Py} = [1 - \text{Gr} - \text{An} - \text{Al} - \text{Sp}] \cdot 100$

Table 3. Calculated and observed compositions (in molecular per cent) of 26 garnets according to the formulae in Table 1.

No.	Gr <sub>calc.</sub>	Gr <sub>obs.</sub>	Δ Gr	An <sub>calc.</sub>	An <sub>obs.</sub>	Δ An	Al <sub>calc.</sub>	Al <sub>obs.</sub>	Δ Al	Sp <sub>calc.</sub>	Sp <sub>obs.</sub>	Δ
1	73.05	92.48	19.43	7.35	0.68	-6.67	8.20	4.31	- 3.89	-5.05	0.26	
2	71.58	64.10	- 7.48	21.38	26.10	4.72	-1.12	4.85	5.97	-6.76	3.07	
3	51.19	51.85	0.66	4.17	10.48	6.31	23.88	19.89	- 3.99	3.85	17.69	1
4	27.61	28.68	1.07	- 1.85	-	1.85	42.68	52.37	9.69	13.87	14.37	
5	17.54	9.65	- 7.89	- 2.02	0.80	2.82	48.96	12.22	-36.74	17.76	72.83	5
6	6.61	0.73	- 5.88	- 3.61	-	3.61	56.80	33.82	-22.98	22.21	65.45	4
7	2.31	10.60	8.29	-10.71	0.15	10.86	64.60	73.62	9.02	25.01	4.61	-2
8	4.03	6.95	2.92	- 7.87	-	7.87	61.48	75.65	14.17	23.89	2.22	-2
9	11.77	-	-11.77	4.91	8.92	4.01	47.44	19.30	-28.14	18.85	70.90	5
10	- 0.88	4.18	5.06	0.48	7.70	7.22	58.40	60.94	2.54	24.42	23.30	-
11	4.28	-	- 4.28	9.00	5.55	-3.45	49.04	16.70	-32.34	21.06	75.90	5
12	27.50	26.70	- 0.80	47.34	66.71	19.37	6.92	3.91	- 3.01	5.94	1.55	-
13	-11.81	13.09	24.90	- 1.11	-	1.11	66.24	58.37	- 7.87	28.87	25.95	-
14	17.68	18.85	1.17	64.04	68.53	4.49	0.76	7.64	6.88	7.00	3.57	-
15	19.40	20.62	1.22	66.88	73.01	6.13	-2.36	4.92	7.28	5.88	0.67	-
16	6.14	12.07	5.93	77.90	76.90	-1.00	-2.28	4.18	6.46	9.18	6.52	-
17	39.40	35.19	- 4.21	1.16	11.24	10.08	33.28	45.13	11.85	8.86	0.92	-
18	24.17	27.29	3.12	- 7.53	6.77	14.30	48.92	50.32	1.40	16.11	0.10	-1
19	13.49	-	-13.49	7.75	0.82	-6.93	44.32	29.24	-15.08	17.73	69.35	5
20	- 0.88	0.74	1.62	0.48	-	-0.48	58.40	74.08	15.68	24.42	19.97	-
21	15.82	-	-15.82	- 4.86	2.11	6.97	52.08	73.20	21.12	18.88	4.32	-1
22	27.61	23.96	- 3.65	- 1.85	1.50	3.35	42.68	54.17	11.49	13.87	5.09	-
23	- 1.74	0.89	2.63	- 0.94	-	0.94	59.96	85.84	25.88	24.98	4.51	-2
24	1.70	-	- 1.70	4.74	1.48	-3.26	53.72	75.00	21.28	22.74	15.63	-
25	20.12	19.10	- 1.02	2.24	9.80	7.56	44.28	57.40	13.12	16.08	0.20	-1
26	- 2.60	0.80	3.40	- 2.36	0.80	3.16	61.52	69.30	7.78	25.54	28.50	

Nos. 1-16. FRIETSCH, R. (1957), Determination of the Composition of Garnets without Chemical Analysis. *Geol. För. Förh.*, 79, 45.

Nos. 17-24. FLEISCHER, M. (1937), The relation between chemical composition and physical properties in the garnet group. *Am. Min.*, 22, 754-755 and 757.

No. 25. PABST, A. (1955), Manganese content of garnets from Franciscan Schists. *Am. Min.*, 40, 920.

No. 26. PABST, A. (1938), Garnets from vesicles in rhyolite near Ely, Nevada. *Am. Min.*, 23, 103.



Table 4. Calculated and observed composition (in molecular per cent) of 26 garnets according to the formulae in Table 2.

No.	Gr <sub>calc.</sub>	Gr <sub>obs.</sub>	Δ Gr	An <sub>calc.</sub>	An <sub>obs.</sub>	Δ An	Al <sub>calc.</sub>	Al <sub>obs.</sub>	Δ Al
1	81.47	92.48	11.01	7.56	0.68	-6.88	7.07	4.31	- 2.76
2	71.09	64.10	- 6.99	28.05	26.10	-1.95	2.23	4.85	2.62
3	52.09	51.85	- 0.24	8.66	10.48	1.82	23.52	19.89	- 3.63
4	32.99	28.68	- 4.31	2.72	-	-2.72	48.93	52.37	3.44
5	22.22	9.65	-12.57	-10.95	0.80	11.75	17.30	12.22	- 5.08
6	6.27	0.73	- 5.54	4.93	-	-4.93	38.40	33.82	- 4.58
7	12.13	10.60	- 1.53	4.89	0.15	-4.74	81.39	73.62	- 7.77
8	14.63	6.95	- 7.68	2.65	-	-2.65	77.92	75.65	- 2.27
9	10.42	-	-10.42	1.99	8.92	6.93	23.27	19.30	- 3.97
10	5.54	4.18	- 1.36	4.81	7.70	2.89	65.51	60.94	- 4.57
11	8.54	-	- 8.54	1.33	5.55	4.22	19.50	16.70	- 2.80
12	33.49	26.70	- 6.79	53.22	66.71	13.49	16.88	3.91	-12.97
13	-0.97	13.09	14.06	- 0.63	-	0.63	69.85	85.37	-11.48
14	25.45	18.85	- 6.60	67.74	68.53	0.79	7.69	7.64	- 0.05
15	25.99	20.62	- 5.37	71.88	73.01	1.13	6.17	4.92	- 1.25
16	17.67	12.07	- 5.60	78.79	76.90	-1.89	1.99	4.18	2.19
17	44.99	35.19	- 9.80	7.49	11.24	3.75	45.78	45.13	- 0.65
18	36.35	27.29	- 9.06	- 4.46	6.77	11.23	61.10	50.32	-10.78
19	10.76	-	-10.76	5.00	0.82	-4.18	21.00	29.24	8.24
20	5.54	0.74	- 4.80	5.87	-	-5.87	67.23	74.08	6.85
21	22.42	-	-22.42	1.16	2.11	0.95	65.88	73.20	7.32
22	36.69	23.96	-12.73	1.64	1.50	-0.14	50.69	54.17	3.48
23	5.47	0.89	- 4.58	6.01	-	-6.01	79.38	85.84	6.46
24	25.09	-	-25.09	- 4.74	1.48	6.22	49.23	75.00	25.77
25	36.91	19.10	-17.81	1.76	9.80	8.04	53.16	57.40	4.24
26	-2.54	0.80	3.34	5.15	0.80	-4.35	68.50	69.30	0.80

tically impossible to determine andradite-spessartite (4 unknowns) with only the help of the unit cell length and the refraction of the mineral. Also the substitution of  $\text{SiO}_4$  by any  $(\text{OH})_4$ ,  $\text{KAlO}_4$  etc. in a garnet may probably alter the physical properties. Moreover, errors in the chemical analyses and the physical determinations provide a reason.

It seems therefore clear that regression equations or the corresponding diagram<sup>1</sup> for the determination of the chemical composition of a garnet do not possess such an order of reliability that they could be used for petrogenetical problems as long as a fair degree of exactness is required.

The regression equation was solved with a digital computer (BESK) by the method of least squares in accordance with the Gauss elimination method. The average error was calculated in accordance with the formula:

$$\left( X_{i, i+2} \cdot \frac{V^2}{m-n} \right)^{\frac{1}{2}}$$

<sup>1</sup> Sriramadas (1957) among others has put forward diagrams for the determination of the chemical composition of garnet as a function of the unit cell length and refraction using Skinner's (1957) determinations of the unit cell length and refraction for the end-members of the garnet group as a foundation. The diagrams show that definite information concerning the chemical composition of garnet is not possible using these principles.

Å. HENRIQUES, *On the determination of the composition of garnet without chemical analyses*

where  $X_{i, i+2}$  is the diagonal element belonging to  $X_i$  in the diagonal element of the inverse matrix.

#### ACKNOWLEDGEMENT

The author wishes to convey his thanks to Prof. F. E. Wickman for his critical reading of the manuscript.

#### REFERENCES

- FRIETSCH, R. (1957), Determination of the Composition of Garnets without Chemical Analysis. Geol. För. Förh., 79, 43–51.  
SKINNER, B. J. (1956), Physical Properties of End-Members of the Garnet Group. Am. Min., 41, 428–436.  
SRIRAMADAS, A. (1957), Diagrams for the Correlation of Unit Cell Edges and Refractive Indices with the Chemical Composition of Garnets. Am. Min., 42, 294.

Tryckt den 24 februari 1958

Uppsala 1958. Almqvist & Wiksells Boktryckeri AB

## Fundamental argument in cenozoic geology dynamic factors: Crustal undulations, thermal dilatation and constriction

By NILS H. ODHNER

Studies of Quaternary shell banks on the Swedish West Coast in the years about 1918 led me to publish an explanation of the geological origin of these banks as a product of biological conditions influenced by land upheaval as well as currents in sea and outstreaming melt-water from the ice sheet (cf. Odhner 1918, 1927, 1930, Hessland 1943). Further thinking on the fundamental causes of these processes gave rise to my constriction hypothesis of 1934, which has brought new aspects to important geological problems and therefore is worthy of attention and discussion.

Many different theories have been established in order to explain the movements in the earth's crust which are one of the fundamental problems in Geology. Nevertheless this problem seems to be far from solved, perhaps because it is too comprehensive for analyses on the basis of present knowledge, in other words is taken up too early and with insufficient argument. Or again, a second alternative seems reasonable, namely that our thinking has happened on the wrong track and led into a blind alley from which the only way out again is to make a reconsideration of fundamental facts.

In such a case the question of course immediately arises which these facts may be, and if this is not decided, we soon end in idle speculations. Better then to try to begin with the best known conditions nearest in geological time, as far as they have been explored. In order to get some starting point, therefore, how would it be to ask instead about the actual changes which took place at the end of the Tertiary and were perhaps the direct causes of the coming Glacial period? This question, it is true, has been answered differently, but two of the Northern geologists who have studied the Scandinavian glaciation with both great care and great success, have published a couple of papers seemingly serving as a valuable starting point for our present theme. The prominent Swedish geologist G. De Geer maintained (1911) on persuasive grounds that an upheaval took place in the mountainous environs of the North Atlantic during the late Tertiary, and that in this connection their central sea basin exerted a pressure on the subjacent masses forcing them to erupt in the surroundings. Some time afterwards (1924) the renowned Finnish geologist W. Ramsay presented with his relief theory (1911) the opinion that it might have been this very over-elevation in the Northern regions during the late Tertiary that directly caused the glaciation there and thus initiated the Glacial epoch. Here it should be added that similar over-elevations of highlands with a glaciation as sequence, and also of low lands without this sequence, occurred in different parts of the world (e.g. in the West Indies according to Willis 1932) at the same time (for closer information

consult Manuals); they were consequently a general phenomenon with no doubt common general cause.

Once upon a time the so-called contraction theory was thought to be able to explain changes like those in the crustal topography and relief, but its importance in this respect has been definitely disproved; I only need to quote Dacqué (1915, p. 113), who writes (in translation from the German): "To make the tangential pushing and pressing powers emanating from the postulated earth contraction responsible for the crustal movements up and down, is dismissed by Andrée (1914) in his recent publication on the mountain building."

With better confidence and results we can now use the persuasive opinions delivered by the two Northern geologists mentioned; since long founded on abundant experience and long research they well merit our attention though they seem to have been forgotten by later authors. Their statements in reality open possibilities for a judgment about immediate causes in the form of active forces influencing and evoking the geological events at the turning-point between Tertiary and Quaternary epochs.

From both the scientists mentioned we learn that an upheaval of geanticlinal parts of the crust had been established, and De Geer also maintained a sinking of the Scandic geosyncline amidst them. No force can be common to these diametrically opposite effects other than the heat from the earth's interior. If we compare the geanticlines with a technical positive vault or more simply an arch bridge, and the geosyncline with the cables of a suspension bridge, we find that an increase in temperature augments their curvature bringing the surface of the arch bridge to a somewhat higher level, the suspension bridge, on the contrary, to a somewhat lower road level. A decrease in temperature brings about the reverse effects. The same influences are exerted on the earth's crust; it goes without saying that the increase of heat comes from the earth's interior, the decrease from absorption by external media such as ice or cold water.

Reasoning in this way we find that the temperature force is mighty enough to cause the movements in the earth's crust exemplified above. No additional factor in the form of loading masses or release from them are necessary to provoke a dynamic effect, and also merely a simple reflection is sufficient to assess this superiority of the temperature force. Likewise we conclude that it is unnecessary to explain a depression of a glaciated anticlinal land as caused by the *load* of the ice sheet; it is quite sufficient to interpret the sinking of the geanticline as a consequence of its *cooling* from the ice sheet. Another remarkable consequence of this reasoning is that the earth's crust behaves during long geologic periods in the same way as every solid body does to the change of temperature. We shall return to this rule below and now pass on to another remarkable consequence of the above-mentioned geological observations and conclusions by De Geer and Ramsay.

Here it may be suitably stressed that De Geer's conclusions about the circumstances of the Scandic upheavals have been entirely corroborated by later investigations in Greenland. Lauge Koch says in his work of 1935, p. 149: "De Geer (1911) forderte eine allgemeine tertiäre Landhebung in allen Gebieten rings um den Skandik. 1921 glaubte Koch, dass dies für Grönland sehr übertrieben sein müsse und rechnete damals nicht mit einer sonderlich starken Hebung in tertiärer Zeit. Spätere Untersuchungen ergaben jedoch, dass innerhalb dieses Zeitraumes sehr mächtige Hebungen in Verbindung mit starkem Vulkanismus und ausserordentlich starken Verwerfungen stattgefunden haben müssen."

We have seen that the over-upheaval of highlands and over-deepening of ocean



basins were a simultaneous effect of the common dilatation by heating in the earth's crust, and that the former phenomenon was world-wide; and so the latter one must have been too. This over-deepening must have caused an accumulation of water from the littoral regions or margins of the continents, which were laid bare and eroded by rivers—especially when the subsequent heavy rainfalls set in during the beginning of the Glacial epoch. It is a natural consequence of these mighty forces that the erosions were on a large scale and in equal proportions to other contemporary phenomena, thus much more striking than similar ones are generally in our days.

As time passed, the glaciation grew more extensive, the ice sheets cooled the highlands, constricted them and thus caused them to sink; cool melting water covered the ocean bottoms, thus constricting their crust and restoring their original shallower depths (because of yielding to the then prevailing counterpressure from the sub-crustal masses), and from all these processes a new displacement of the water masses followed in the form of a transgression drowning again the drained coastal zones together with their mighty river furrows, which after this event are represented in the so-called submarine canyons; these are in most cases continuous with actual river valleys; their origin is, consequently, as already explained in this way by me in 1934, in full agreement with Shepard's later opinion, independently given in 1953. A phenomenon difficult to explain was in every case their great depth of submergence, but we must not forget that the transgressing masses of cool water likewise constricted the marginal zones of the continents forcing them to submerge actively in addition to their passive inundation; their actual depths thus are enormous from a general point of view but not inexplicable with the present way of reasoning, that of the *constriction principle*.

We now have seen examples of *constriction*, as I have named already in 1934 the thermal diminishing by cooling in *superficial* dimensions (in contrast to *contraction* or a similar diminishing in *radial* direction, as I restrict it in accordance with the meaning of the old contraction theory). We found occasion just now to speak of marginal constriction along a coast line of a continent or an island, as soon as these zones are constricted by cold water masses; this phenomenon plays some role as leading to total constriction in large areas, e.g. ocean bottoms. See further thereof in Odhner 1944, 1948a.

The last-mentioned state of total constriction has affected the Mid-Atlantic Ridge, from the beginning a supramarine mountain chain, and similarly the Lomonosov Ridge in the North Polar basin newly discovered by the Russian scientific expeditions (cf. Ahlmann 1955). As mentioned above, the Mid-Atlantic Ridge was explored by the German Meteor Expedition, and its variously sculptured relief proves its supramarine origin. L. Kober, the Vienna geologist, expressed as early as in 1912 the opinion that the Mid-Atlantic Ridge is a sunken young mountain ridge (l.c. p. 232), and he was even far-sighted enough to suppose an "Orogen" between the New Siberian Islands and Ellesmere Land dividing the Polar Basin and representing the later detected Lomonosow Ridge (cf. Kober 1912, p. 237). That the Mid-Atlantic Ridge has been situated above the sea but was submerged later in Glacial time was stated by Malaise (1945, 1951) on the diagrams given by Piggot (1938) displaying a difference on each side of the now submarine ridge. Malaise reported recently (1956) even a sinking in another part of the Mid-Atlantic Ridge, namely in N.  $5^{\circ}45'$  W.  $31^{\circ}43'$ , where the Swedish Albatross Expedition 1948 took, on its station 234, a core from 3577 m depth. In this core Dr. R. W. Kolbe, who examined the diatoms in all the cores taken by the Expedition in the tropical Atlantic, detected a horizon containing

exclusively fresh water diatoms (cf. Kolbe 1955, Malaise 1956). Kolbe (1955, p. 159) says about the local flora: "Apart from the everpresent *Melosira annulata* not less than 17 other freshwater species could be noted." The presence of these he thinks to be due to transport from the large African rivers (p. 160). This supposition may be true, but the present currents, as Malaise (1956, p. 121) emphasizes, run in a contrary direction, so that it has relevance only to remote times, when these lands were about 4000 m more elevated than now. It may be added that none of the other cores examined by Kolbe had the same suitable conditions for forming a lake as this one, either they show too great a depth or are situated on the African continental slope too steep for any lakes to arise. Certainly, however, many other lakes seem to have existed on the Mid-Atlantic mountain ridge judging from the map published by Stocks (1934).

It has been remarked against the above opinions (comprised as the constriction theory) that they are nothing but a reiteration of the old and abandoned contraction theory. This objection, however (expressed in a private letter to the author), is not at all correct, as we have found above. The difference is verified in the ways both theories explain the orogenesis. According to the contraction theory this process should be a consequence of tangential stresses and their assumed pressing upwards of subcrustal masses in a geosyncline. The constriction principle, on the contrary, lays stress upon the pressure from below that we have found to be the consequence of the crustal expansion through heating within the geosyncline. Of course, a heating of the crust cannot pass on indefinitely, because the heating and depression of it is ended by its final weakening; then the whole process is reversed and the counterpressure from below prevails in pushing up the former solid vault as the primitive fold of an orogen. There is nothing else in the present theory that separates it from other modern opinions on mountain building (e.g. those advanced by Kober 1921), but there may be stressed two new aspects on the orogenesis: first the so-called convection currents in the deep subcrustal masses ("Unterströme" Ampferer's) are superfluous, as merely wholly hypothetical, for explaining the process; and secondly: the residual geosynclines (German: Restgeosynklinale, cf. v. Seidlitz 1931, p. 189) outside the orogen folds in some submerged mountain strikes on the Indian and Pacific Oceans, gave rise to important new geological appearances. Some residual geosynclines (e.g. on the south side of Java) were, in Glacial time, due to their sites, filled up with the cold ocean water cooling and constricting its environs, that is on the one hand the margins of the orogen (Java), on the opposite side the original bordering anticlinal land (bottom of Indian Ocean). The latter had first been subject to total constriction, the orogen then to the still actual marginal constriction, and the bottom of the residual geosyncline therefore was subjected, during its cooling, to a tearing in opposite directions, opening between its two slopes a fissure steadily increasing in depth and width (cf. Odhner 1948a). In this way the deep sea "grabens" are explained much more simply than through the opinions of Suess 1909 (cf. Tams 1922, p. 240), based on isostatic ideas on pressing down lighter sial into heavier sima, thus forming hypothetic "roots of mountains" to answer for the gravity defect in the graben; such roots have been contradicted by Bowie (1924) and Bucher (1933). Other residual geosynclines were shut off from the cold oceans and beheld their water relatively warm and their bottoms U-shaped, because not teared by temperature stresses (as "Saumtiefe", cf. Stille 1957 in contrast to negative so called Meinesz-Zonen; they show positive anomalies).

If we tarry a moment at these orogenetic zones, we find further an explanation to

their great number of volcanoes in the circumstance that there is a pressure on the islands exerted by the marginal constriction (and directly causing the positive anomalies just off the coast) which, as I pointed out in 1948, drives the subcrustal masses landwards and lets them out there, forming a chain of inland volcanoes, where the gravity in the anticline is lesser, because it is warmed from below being sited on the continental shelf and far from the cold ocean deep (cf. Odhner 1948a). Impulses to earthquakes moreover are issuing from the deep fissures of the grabens as well as from the basins with positive anomalies, and it seems as if these fissures penetrate deep down and even horizontally, and may cause the seismic activity even in depths under the continents down to 700 km.

In the East Indian Archipelago most of the residual geosynclines have high negative regional anomalies,<sup>1</sup> because they are cooled by the chilly waters from the free Indian or Pacific Oceans. This cooling causes in the residual geosynclines, as mentioned above, a tension between marginal constriction of the south coasts of the garland Sumatra–Java–Flores and the total constriction of the Indian Ocean bottom. This process began in the Ice Age with the transgression and influx of cold water from the open oceans and transformed residual geosynclines to deep troughs and grabens all round the world. The zonal gravity anomalies of the crustal topography in the Sunda regions, so excellently worked out and published by Vening Meinesz (1934) show this thermal and crustal dependency with much evidence. The anomalies explained in this way are understood more logically and persuasively than from the isostatic “buckling hypothesis”, which postulates lighter masses being depressed downwards into heavier ones for explaining decreasing anomalies. A criticism like this in accordance with the constriction and dilatation principle (constriction theory) is in full accordance with the facts shown by Gerth (1951). He finds from a comparison of the negative gravity anomalies in the West Indian and the East Indian Archipelagoes that they do not always coincide with the orogenic zones but sometimes even cross them or lie in the forelands, thus demonstrating a contrast between the real conditions and their explanation through the buckling hypothesis. Gerth restricts himself to showing this inconsistency and gives no other explanation. In reality, however, the actual *distribution of warmth* in the earth's crust is responsible also for this difference in the gravity anomalies. The glacial and still remaining cooling (absorption of the crustal warmth by the cool waters) in the residual geosynclines, on the one hand, and the still proceeding heating of those anticlines which are under the lee of this cooling, on the other hand, is no doubt responsible for high negative anomalies in both the regions in question. Their orogenetic nature does not influence the phenomenon. This is convincingly proved by the *high positive* anomalies in both of the archipelagoes, e.g. in the Banda Sea and the Caribbean Sea, which both are considered by the geologists, and even not least on biogeographical grounds, as sunken lands which nowadays are still locked away from open ocean and thus contain a persistent warmth in their crust.

In reality, the above-mentioned examples prove, however, that both those causes for the origin of gravity anomalies are relevant and can even be variously combined. Consequently, the negative anomalies may be due either to dilatation at heating and thus diminishing of the specific weight, as in mountain chains, or to tension and even breaking within the earth's crust, as in deep grabens. Positive anomalies also may have a double cause; in some cases they arise on account of cooling and constriction

<sup>1</sup> These are called isostatic but unjustly, since they are not dependent on isostasy.



which increase the specific weight of the crustal masses, in other by means of addition of material from the environs (intrusion of magmas); both these factors may co-operate at sinkings of volcanic islands, and in such cases the anomalies attain extreme positive values. These points of view should be noticed when interpreting gravity anomalies. They show the dominating importance of thermal states and changes, that is, the principles of the constriction theory, for understanding the crustal movements. In this light it is evident that the postulated influence of loading or isostasy in general has been highly overestimated, because these are, evidently, wholly negligible.

The Philippine graben is morphologically more complicated than the Java graben, as proved by the extensive echo-soundings made by the Danish Galathea Expedition and reported by A. Kiilerich in Ymer 1957. The graben is formed in connection with the Tertiary folding zone, says this author (p. 208) and emphasizes further the repeated earthquakes on the western continental slope (l.c. fig. 9). These indicate a mobile zone of the crust where a marginal constriction is exerted. East of the graben, the total constriction has befallen the bottom of the whole Pacific, and thus a tearing within the residual Philippine geosyncline has caused the fissure in its bottom. The origin of this graben thus agrees with that of the Java graben, but the morphology is perhaps more elaborated on its east side. The transverse furrows on these slopes may possibly be original transverse fissures, on a Tertiary coast sunken on account of the total constriction, whereas the western slope is even and grows steadily steeper by means of the orogenic upheaval and the abyssal sinking. The Danish investigations, moreover, make evident that stones and sediments from the steep slopes are steadily depositing thus filling up the fissure proper and the base of the slope by which the original V-profile of the graben may be changed to a more U-shaped one, and vice versa when the graben is deepening; the two kinds of grabens discerned by Kuenen (1934), can therefore pass into each other.

The fact that several similar deep grabens exist in the Pacific, on the outer sides of many island groups, seems to indicate that a development of the residual geosynclines in different orogens took place in a similar way during the glacial time. More exposed synclinal folds were easier subjected to the constriction than those more sheltered by large islands or continents in the lee or at the front of cool ocean basins. This process was in common with the large oceans; in the Atlantic the West Indian islands and the South Antillean chains witness for great sinkings of lands due to similar causes as in the Pacific. Certainly further investigations of the Pacific bottom will bring about more support to such conclusions, which are in agreement, too, with biogeographical facts of land submergences exemplified below.

We now leave the pure geological and geophysical phenomena combined with the thermal processes already mentioned and explained in new ways; others, such as the coastal gravity aberration, corroborate the above-mentioned. We now pass to another scientific field of facts also dependent on the same processes because of their geological and geographical importance. Biogeography gives us indications about the past geomorphology of lands and oceans, and some changes in that respect may be given on account of biogeographical conditions as an illustration of the probability of the much discussed land connections in remote times.

I published in 1923 a paper on these phenomena in dealing with molluscan distribution on the West coast of Africa. In order to explain the biogeographical problems met with in that connection, I made the supposition that the submarine ridges on the Atlantic bottom had once been supramarine connections mediating the distribution of e.g. identical species in now separated localities on opposite sides of the ocean.



On page 31 of this paper I say: "Other faunistic facts mentioned above support the assumption of former land areas with an extension in north-southern direction, and these may perhaps, in some part, remain as the S. Atlantic threshold, and as the banks off S.W. Africa."

It was therefore not unexpected but quite in accordance with my previous opinion about former lakes on the Mid-Atlantic chain, to find evidence of such a connection in the core 234 taken by the Swedish Albatross Expedition related above. I therefore interpret this interesting find as a good proof of my theory advanced in 1923 concerning the now submarine ridges as once supramarine land bridges and as an evidence of the correctness of my later (1934) established constriction theory and its thesis that the earth's crust reacts according to the same rule as every solid does on temperature changes.

Some of the best examples of other submarine ridges having caused the same facts are the now submarine connections between S. America and the Antarctic continent as well as similar presumptive ones to different islands in the environs of the Antarctic. Mortensen (1910), who examined and described the Echinids from these regions collected by the Swedish Antarctic Expedition 1901–1903, concluded that their distribution demonstrated "a former connection between South America and the Antarctic continent; especially the occurrence of the viviparous genus *Abatus* in both these regions is conclusive evidence of such a connection". A similar connection should have existed to Kerguelen Isl., because "especially the *Abatus* species being viviparous and a littoral species, cannot possibly have come to Kerguelen over vast deep sea now separating this group of islands from South America". On this occasion I want to give a quotation from my paper of 1944 on Nudibranchs and Scaphopods of the Norwegian expeditions 1927 and later, where I say (p. 35) in agreement with the above statements:

"Conclusively, the distribution of viviparous animals in the first place, and probably also the above-mentioned *Isometra vivipara*, and *Cadulus dalli* as well, can be satisfactorily explained only by assuming a migration along a continuous bridge between S. America and Graham Land over the Falkland Islands, S. Georgia and the island groups farther to the South, that is by means of the so-called South Antillean Arch. As to the existence of this postulated bridge, which, of course, enabled the distribution of many other organisms, terrestrial as well as marine, plants as well as animals—I restrict myself merely to quoting two Swedish authors for this theme: Du Rietz 1940 and Ander 1942—a statement of Th. Stocks (1932, p. 198) is of a great interest. In dealing with the echo soundings of the Meteor Expedition in the South Atlantic, Stocks says: "Eine untermeerische Verbindung zwischen Südamerika und den Südshetland-Inseln im Zuge der Shag-Felsen, Südgeorgiens, der Südsandwich- und der Südorkney-Inseln ist nach unserer heutigen Kenntnis nicht zweifelhaft".

These zoogeographical and oceanographical facts have been corroborated nowadays by geological data established by Høltedahl, the distinguished Norwegian geologist. I take the liberty of quoting a piece from Skottsbjerg's recent (1956) book on Juan Fernandez, where he says (p. 389): "In his important paper of 1929 Høltedahl has shown that the old idea of land connection between Tierra del Fuego and Graham Land (Palmer Peninsula) by way of the Burdwood Bank, Shag Rocks, South Georgia and the South Sandwich and South Orkney Islands, which had been doubted by some, holds good; we have to do with a mountain range, a continuation of the South American Andes, bordered by deep water which, on the Pacific side, has the character of an abysmal trench but which exhibits old sediments to such an extent that we

are forced to postulate land where there is now deep sea. The South Sandwich Islands, being entirely neovolcanic, have the appearance of an "oceanic" archipelago, but they were built up during late Tertiary times over an older foundation—a parallel to the history of Juan Fernandez and many other islands."

That sinkings to great depths have to be accepted in spite of resistance from scientists, is thus admitted by modern geologists. One further quotation from Høltedahl may be given for illustrating this fact; he says (cf. Odhner 1944, p. 37): "The common occurrence of well marked ridges or rises (and corresponding narrow depressions) shown by the more recent, detailed soundings in the Atlantic is a feature of great interest to geology. We see now in the relief of this oceanic area a pattern that reminds us more of that of the continents than previously was thought to be the case. As we may, in the continents, see the products of *various* periods of orogenic movement expressed in the present relief, so may some of the sub-oceanic ridges follow the trend of folding zones also of remote geological time. An example of this type is the Newfoundland ridge. These features, like so many others, speak against the idea of permanency of oceans and continents, and against the view of oceanic and continental areas being of fundamentally different structure and history at least as far as the Atlantic Ocean is concerned ... With their large amount of terrigenous, clastic sediments etc. the South Orkneys and also South Georgia agree with the folded ranges of the continents. In fact, in order to explain the existence of these masses of sediments we must necessarily *assume land to have been present where there is now deep sea.*"

Under such circumstances it is quite strange to find geologists, oceanographers and biologists still adhering to the old theory of permanency of the oceans and not even believing in sinkings of land strips or islands. Or, perhaps this unrealistic opinion is held only with respect to the Atlantic Ocean? There is however, after the publication of Hamilton's analysing work on the guyots (March 1956), no doubt any longer about the reality of land submergences in the Pacific. It is true that the sinking of the guyots in question is dated to the Cretaceous and limited to a depth "below the zone of reef-coral growth; finally they sank to the present depth" (700-900 fathoms), so that they have perhaps no other relevance to the cenozoic geology than to stress the possibility of submersion in general, which, however, is important enough and serves to verify the opinions expressed here. Hamilton's work, therefore, is of great importance for the present aim of research. There is only one point of view of its author that I cannot share, and I think we have reasons to refute his maintaining on p. 1, that his findings "refute the hypothesis of trans-oceanic "sunken continents" used to explain faunal migration, at the same time suggesting the possibility of "island stepping stones". To this point of view I wish to object the following argument.

On p. 1 the author says that "the Mid-Pacific Mountains are a great submarine mountain chain", and I find nothing that might contradict his opinion. But this same fact implies that the chain must have arisen in a similar way to every other orogen of this kind, that is from a geosyncline, and such a geologic formation presupposes the earlier existence of one bordering geantiline at each side. In such a case, however, we had already in them the transoceanic land connections needed for organisms and being, furthermore, a much better means for that purpose than the "stepping stones" which according to Hamilton (after Zimmermann 1948, who is, however, not quoted) had alone to fulfil this function. Of course, the latter *could* have rendered some service in that respect especially to flying organisms or marine

forms with pelagic larvae, this should not be denied, but it should be kept in mind that a generalization of the "stepping stone" spreading to let it replace continental dispersal is unrealistic and far from acceptable to Biology and directly disproved by Geology. Sunken continental lands in the shape of bordering anticlines along orogens have been postulated by several geologists (see below). I quote also here Du Rietz 1940, who speaks about bipolar distribution of plants, though the same consideration is relevant also for every transoceanic relation: "That bipolar distribution is not dependent on the Alpine Orogen, is shown by the African bipolar units and their connecting tropical mountain populations on epeirogenetic highland fragments ... To explain the facts of bipolar plant distribution it seems necessary to look for epeirogenetic transtropical highland bridges older than the mountain-chains of the Alpine Orogen. Such highland bridges may have existed not only in Africa, but also bordering the transtropical Alpine geosynclines (i.e. the Andean and the Malaysian geosynclines), partly passing over the present deep sea bottom." Such a bordering land is also a scientific demand e.g. all along the West coast of N. and S. America, as both Kober (1921), Gregory (1930), Born (1933) and Joleaud (1934) have emphasized. Skottsberg who is mentioned among the authors criticized by Hamilton (l.c. p. 51) is therefore on safe ground in his defence of these and other continents in the Pacific Ocean, where, as some preliminary newspaper notices now and then report, a much more broken bottom than expected has been found by recent exploring expeditions. Therefore also statements of biogeographical contents, if they are founded on sufficient geological base material, are to be considered as quite reliable; the criticism against older opinions of land bridges should not go so far as to condemn everything of that sort in favour of speculations of the "stepping stone" type. Therefore, and on my own experience as a malacologist, I can only agree with Skottsberg in his opinion about sunken continental land in the Pacific. As an example of a sound view of such a problem I want to quote Skottsberg (1956, p. 384), when he, in concordance with Brügger, describes the late geological history of the Juan Fernandez Islands, "facts which open wide perspectives to the biologist", in the following picture:

"Brügger begins by stating that 'el mar del Eoceno' ended somewhere in the latitude of Arancu (38°), because a continental mass, 'la Tierra de Juan Fernandez', still existed (p. 50), and pp. 56-59 he relates the history of this land. North of Rio Maullin (about 42°) is a zone of dislocations foreign to the structure of the Andes, and this zone coincides with the direction of a broad submarine ridge which branches off from the continent; on this ridge are situated the Juan Fernandez Islands and, farther north, San Ambrosio and San Felix. Taking the 2000 m curve as a boundary, the ridge extends south to the Magellan Straits; we observe e.g. in the island Diego de Almagro the same northwest direction that we find in the Tertiary deposits of Parga and other places in the zone north of Rio Maullin. To this must be remarked that the 2000 m line surrounds the Chaigneau ridge and that in order to unite it with West Patagonia the 3000 m curve has to be used. This is also seen from Brügger's map, probably copied from Supan. The absence of marine sediments of Eocene age shows (p. 59) that the Juan Fernandez land was, at that time, united with the continent, but that, during the Oligocene, subsidence set in is evident from the extension of the marine Navidad series south to 45°, and this was, as we have heard, referred to Upper Oligocene or Lower Miocene. Also after the separation the Juan Fernandez land continued to exist until finally, presumably with the late Tertiary uplift of the Andes, the last rest disappeared, but not before considerable magma ejections had given birth to the two archipelagoes. To judge from the degree of denudation and in



view of the recent volcanic activity close to Masatierra and on San Felix the islands are young, probably Pliocene, when there still existed a rest of the old Tierra de Juan Fernandez, where the Eocene flora immigrated. When, however, this remnant later on perished, there remained only the volcanic parts forming the actual Juan Fernandez Islands, which served as refuges of the flora."

In my paper of 1950 on the Galapagos Bulimulids similar opinions were set forth: I quote the following pieces (from p. 266): "If we exclude the litoral Auriculids (Ellobiids), the terrestrial mollusc fauna of the Galapagos Islands contains nearly 100 % endemists. This circumstance speaks in favour of ancientness of the fauna and its origin by means of natural dispersal, that is along continuous land connections."

"On the other hand, no direct proof of land bridges is available. The Galapagos have revealed no traces of continental rocks proving transoceanic connections, and moreover, the great depths surrounding them are generally considered as disproving any connection. These facts have been adduced as proving the origin of oceanic islands and their fauna on the spot and their isolation from their very beginning."

"This conclusion, however, is far from entitled. Already James Cook, when visiting St. Helena in 1771 and finding a species of land shells (probably a *Succineid*) upon the tops of the highest ridges, concluded that it 'probably has been there since the original creation of their kind', unless 'this rock be supposed to have been left behind, when a large tract of country, of which it was part, subsided' (1773, p. 798). From this point of view, that the island fauna is the last debris of an once abundant one inhabiting a larger land, which has been submerged, all facts will be better understood and found to have closer relation to each other."

The argument in these pages has shown that conflicting opinions in cenozoic geology can be adjusted under the following presumptions in conformity with Nature's own conditions: The earth's present crust is constructed as a mosaic of positive and negative undulations (cf. Stille 1913) or vaults reacting to long-periodic changes of temperature. These facts enable us to explain the ever-lasting movements of the crust which are stated by Geology and brought into evidence also by Biogeography. Since the propelling power provoking these movements is derived from the temperature states of the crust and their changes, we may conclude our discussion of the problem in question with a quotation of the geophysical point of view expressed by Sir Harold Jeffreys (1953, p. 117) in the following words:

"The direct evidence, such as rise and fall of the land surface, the distribution of gravity, and mountain formation, is in better agreement with the hypothesis that they are due to temperature changes, mainly cooling, in an ordinary solid."

Lastly, here may be added some reflections on the ice pressure, which has been considered as a *conditio sine qua non* for the movements in the earth's crust, but which is wholly omitted in the sentence just quoted from Jeffreys.

It is a matter of fact that in some newly published papers to which I return below, the ice pressure still dominates. Recurring once more to De Geer's essay of 1911, we found that he dates the upheaval in the North Atlantic environs to the Late Tertiary. But in the same pages he also confesses his belief in Jamieson's ice pressure theory of 1865, though a scrutiny would no doubt have convinced him of the inconsistency of the two opinions. Evidently he did not reflect on their incompatibility. After his time the same neglect has continued among the authors: they do not observe the dissonance between Late Tertiary upheaval with its specific causes in the absence of immediate glaciation, contrasted with post-glacial upthrusting as caused by sup-



posed ice unloading. Thus it happens that the explanations of these phenomena collide, which leads to confusion.

Without the least doubt the French glaciologist Paul-Emile Victor has performed extraordinary investigations in the icecap of Greenland and succeeded excellently in measuring its thickness in the southern half of its extension (cf. Ahlmann 1955). In 1956 he gave a very interesting report on the results of these epoch-making investigations showing that "Greenland resembles an ice-filled bowl rimmed by coastal ranges" and expressing the opinion that "at one spot the enormous overburden has depressed the bedrock to more than 1200 feet below the sea level" (l.c. p. 131, map explanation). This latter statement, however, seems to be out of agreement with the just-mentioned investigations by G. De Geer, and cannot be, consequently, scientifically defended. The general belief in icepressure as causing a sinking in the crustal substrate is certainly due more to the impression on the human mentality than to a real knowledge of such a process. The substrate of the Greenland ice cap was certainly shaped as a bowl by the same factors that once upthrust the rimming coastal ridges in Late Tertiary times, as De Geer suggested. During the following glaciation the bowl-formed concavity (probably then being still above sea level, since this was so essentially lowered according to the above-mentioned basin deepening) was filled with the ice pouring down from the mountains; this ice could not recede or else vanish, even though the sea level grew higher, since the ice cap was always sheltered all around from being melted on the one hand by the influence of sea water, on the other by climatic changes.

However, a certain effect is certainly to be ascribed to the ice-cap, namely its cooling of the ground. The map published by Victor and still better, the map given by Ahlmann, shows a striking similarity to a West-Norwegian fjord landscape, both in the narrow shape of the valleys and their direction across the length extension of the land. Further, their deepest parties lie in a considerable distance from the coast, close to which the relief is much higher. Briefly, the Greenland picture and the Norwegian fjord-regions have with no doubt a similar origin. The cooling of the ground by the ice-cap caused the deepest fissures under its thickest parts but nearer to the coast, where the warmer sea heated the crust more than farther inland, the fissures could not penetrate so deep, leaving a coastal threshold at the fjord mouths. Thus, even the fjord problem, so long discussed though yet not sufficiently penetrated (cf. Holmes 1947, p. 224-26), finds an unsought explanation by means of the constriction principle.

De Geer (1911) emphasizes the intimate connection between the sinking of the Scandic Basin and the upthrusting of the surroundings with their centrifugal tilting both in East Greenland and Spitzbergen, Scandinavia and Scotland, as well as the mighty outpouring of basalt beds or intrusions on a large scale within wide tracts around the Scandic. His inference, as mentioned above, has been verified by means of later investigations.

The French interpretations as effects of icepressure in Greenland have been accepted for equal conditions in the Antarctic. Thus Dr. J. Kaplan (1957, p. 24) states about the Antarctic ice-cap in the surroundings of the Byrd stations: "Here preliminary seismic soundings suggest that the ice cover of the continent may possibly be 10,000 feet thick at some points. These preliminary readings are surprising, particularly since the measurement site is only 5,000 feet above sea level. This would suggest that there is land some 5,000 feet below sea level. Obviously, these preliminary readings must be checked carefully before any conclusions can be made. While most of

this is probably due to peculiar topographic features, it appears that the weight of ice has undoubtedly depressed the continent in this region to some extent. I might point out that this effect has occurred in Greenland where portions of the interior are also below sea level." It is necessary, though far from pleasant, to draw the attention to these conclusions which lack all scientific proofs. Certainly a scrutinizing reexamination of their tenability will show their prematurity at least, or that their explanation will be the same as here suggested for Greenland. In Tertiary times the Antarctic had a genial climate, was free from ice and connected with near-by continents by means of land bridges (cf. above). The late submergence of those caused a deterioration of the climate and widened the glaciation.

To allay all anxiety it should be said that the question about ice-pressure has, indeed, merely an academical importance and does not at all influence the field investigations during the present IGY.

People have also made the assumption, only as a matter of speculation, that if the remaining ice-caps should melt away, this would lead to terrible inundations all over the world. However—on account of the stability of natural forces—such an eventuality would no doubt imply also an increase in the capacity of the ocean basins, just as was the case during late Tertiary according to the above-mentioned principles of the constriction theory (first published by me in 1934). Therefore, human kind has evidently nothing to fear—if nature only is allowed to mind its own business.

A more detailed criticism of new opinions especially from American authors has been given in the paper of my esteemed collaborator Malaise 1957 with which I agree in essential points.

#### LITERATURE

- AHLMANN, H. W:SON, Forskning och händelser i Arktis efter Vega-expeditionen. Ymer: 75: 2 1955.
- ANDER, K., Die Insektenfauna d. Baltischen Bernsteins nebst damit verknüpften zoogeograph. Problemen. K. Fysiogr. Sällsk. Handl. N. F. 53: 4. Lund 1942.
- ANDRÉE, K., Über die Bedingungen der Gebirgsbildung. Berlin 1914.
- BORN, A., Über Werden und Zerfall von Kontinentalschollen. Fortschr. d. Geol. u. Paleont. X: 32. Berlin 1933.
- BOWIE, W., A Gravimetric Test of the "Roots of Mountains" Theory. Dep. of Commerce. U.S. Coast and Geodetic Survey. Ser. 291. Washington 1924.
- BRÜGGEN, J., Fundamentos de la Geología de Chile. Santiago 1950. (Vide Skottsberg 1956.)
- BUCHER, W. H., The Deformation of the Earth's Crust. Princeton 1933.
- COOK, J., An account of voyage round the world. Hawkesw. Voy. Vol. 3, 1773.
- DACQUÉ, E., Grundlagen und Methoden der Paläogeographie. Jena 1915.
- DE GEER, G., Kontinentale Niveauperänderungen im Norden Europas. Compte Rendu du XI Congrès Géol. Internat. Stockholm 1911.
- DU RIETZ, E., Problems of Bipolar Plant Distribution. Acta Phytogeographica Suecia, 12. Uppsala 1940.
- GREGORY, J. W., The Geological History of the Pacific Ocean. Proc. Geol. Soc. 86, p. LXXII, 1930.
- HAMILTON, E. L., Sunken Islands of the Mid-Pacific Mountains. Geol. Soc. America, Mem. 64, 1956.
- HOLTEDAHL, O., On the Geol. and Physiogr. of some Antarc. and Subant. Isl. Sci. Res. Norweg. Ant. Exp. 1927 etc. Det Norske Vidensk. Akad. Oslo 1929. (Vide Odhner 1944, Skottsberg 1956.)
- JEFFREYS, SIR H., Half a Century in Geophysics. The Advancement of Science, X: 38, 1953.
- JOLEAUD, L., Paléogéographie de l'océan Pacifique. Peuplement des îles du Pacifique. Mem. Soc. de Biogéographie IV. Paris 1934.
- KOBER, L., Der Bau der Erde. Berlin 1921.
- KOLBE, R. W., Diatoms from Equatorial Atlantic Cores. Rep. Swed. Deep-Sea Exp. 1947-1948. Vol. VII, Fasc. III. Göteborg 1955.

- KUENEN, H. v., Relations between Submarine Topography and Gravity Field. In: Vening Meinesz, Gravity Exp. at Sea, Vol. *II*, Delft 1934.
- MALAISE, R., Tenthredinoidea of South-Eastern Asia, Zoogr. Review. Opuscula Entom. Suppl. 4. Lund 1945.
- Atlantis, en geologisk verklighet (Atlantis a Geol. Reality), Stockholm 1951.
- Sjunket Land i Atlanten. Ymer 1956, Stockholm.
- Oceanic Bottom Investigations and their Bearings on Geology. Geol. Fören. i Stockholm Förhandl. 1957.
- MORTENSEN, TH., The Echinoidea. Wiss. Ergebn. Schwed. Südpolar-Exp. 1901–1903. VI Zool. *II*: 4, Stockholm 1910.
- ODHNER, N. H., Contrib. Marine Moll. Faunas of South and West Africa. Medd. Göteborgs Mus. Göteborg. K. Vet. o. Vitt. Samh. Handl. 4, 26: 7. 1923.
- The Constriction Hypothesis. Geografiska Annaler, Stockholm 1934.
- Moll. Nudibranchia and Scaphopoda with zoogeogr. Remarks and Explanations. Sci. Res. Norweg. Antart. Exp. No. 21, Oslo 1944.
- Thermischer Krustaldruck contra Gravitationskontraktion. Petermanns Geogr. Mitt. 1948.
- Les Modific. des Contin. et leurs conseq. biogéogr. Les princip. de la théorie de la constrict. C. R. somm. soc. Biogéogr. Paris 1948 b.
- Studies on Galapagos Bulimulids. Journ. de Conch., XC, Paris 1950.
- PIGGOT, C. S., Core Samples of Ocean Bottom. The Scient. Monthly, 46, Washington 1938.
- RAMSAY, W., Die Reliefhypothese zur Erklärung der Klimaschwankungen. Petermanns Geogr. Mitteilungen 1911.
- The Probable Solution of the Climate Problem in Geology. The Geol. Magazine 61, London 1924.
- SEIDLITZ, W. v., Diskordanz und Orogenese der Gebirge am Mittelmeer. Berlin 1931.
- SHEPARD, F. P., Submarine Canyons. Contrib. Scripps Inst. Oceanogr. Univ. of Calif. La Jolla (1950) 1951.
- SKOTTSBERG, C., Derivation of the Flora and Fauna of Juan Fernandez and Easter Island. The Nat. Hist. of J. Fern. and East. Isl. Vol. 1: 3. Uppsala 1956.
- STILLE, H., Tektonische Evolutionen und Revolutionen in der Erdrinde. Leipzig 1913.
- "Atlantische" und "pazifische" Tektonik. Geol. Jahrbuch, 74, 1957.
- STOCKS, TH., Der Südantillen-Bogen im Lichte neuerer Erkundungen. Z. Gesellsch. Erdkunde, 5, 6. Berlin 1932.
- Atlantischer Ozean, Übersichtskarte der Tiefenverhältnisse auf Grund ... der Lotungen des "Meteor" ... 1934.
- SUESS, E., Das Antlitz der Erde, *III*, 2. Wien 1909.
- TAMS, E., Einführung in die Geophysik. Naturwiss. Monogr. u. Lehrb. 4. Berlin 1922.
- VENING-MEINESZ, F. A., Gravity Expeditions at Sea 1923–32, Vol. *II* (Publ. Netherlands Geodetic Commission). Delft 1934.
- VICTOR, P.-E., Wringing Secrets from Greenland's Icecap in Six Years of Exploration. The National Geographic Magazin. Jan. 1956.
- WILLIS, B., Isthmian Links. Bull. Geol. Soc. America, 43, 1932.
- ZIMMERMANN, E. C., Insects of Hawaii, *I*, 1948.

### Postscript

After the preceding pages had gone to press, my attention was directed to some papers in which Dr. G. M. Lees, late president of the Geological Society of London, expresses opinions which agree with those advanced by me both here and earlier. In order to enable a comparison to be made between our conclusions, I quote below some statements from the publications in question, which are:

Interpretation of Gravity Anomalies. Nature, 169, p. 988, 1952.

The Evolution of a Shrinking Earth. Anniversary Address delivered at the Annual General Meeting of the Society on 29 April, 1953. Quarterly Journal of the Geol. Soc. London, *CIX*, 11 Dec. 1953.

The Geological History of the Oceans, Deep Sea Research, 1954, 1. London.



In the first of these papers one reads:

"In summing up, Dr. G. M. Lees said that in continental areas there are so many exceptions where the isostatic principle does not apply that he doubted its validity. . . . One frequently quoted support for isostasy is the assumption that the recent rise of Scandinavia is the consequence of the disappearance of the great Ice Age ice burden. This is a most unsafe deduction. . . . It is commonly asserted that a sedimentary basin sinks isostatically because of its load of sediments, but, said Dr. Lees, is it not rather that the sinking from some quite different cause has allowed the sediments to accumulate? He believed that crustal deformations are the consequence of contraction of the earth and not of convection currents in an imagined sima."

In his paper of 1953 Dr. Lees says:

"Belief in the permanence of oceans has coloured geological thinking for many decades, but recent physical research has demolished many of the bases on which the hypothesis was founded. I shall attempt a short review of the problem as I see it and shall show that in my opinion there may be no fundamental difference between the basement of the oceans and the continental masses." [Page 233.]

"There is no geological evidence for an assumption that the oceans have been permanent, and there is abundant palaeogeographical evidence indicating extensive continental areas in parts of the present oceans. It is difficult to envisage a mechanism which could have repeatedly compressed the continents into such a complex structure if there were a fundamental difference in both composition and rigidity between oceans and continents." [Page 247; see also Lees 1954, p. 69.]

"Sedimentation is the consequence and not the cause of geosynclines; no adequate reason for the broad geosynclinal depressions has yet been offered. . . ." [Page 251.]

"The geophysical conception that mountain uplifts are compensated by deep roots ignores so many geological facts, and there are anyhow so many exceptions that, in my opinion, the whole interpretative side of gravity surveys requires review and where possible control by seismic investigation." [Page 254.]

Lastly, the following statement may be cited from Lees 1954, p. 69:

"A boring in 1952 on Eniwetok Atoll, Marshall Islands, which may be considered as a sea-mount which has managed to remain at the surface by sedimentation keeping pace with the subsidence, encountered basalt at 4,208 feet below sea level, under shallow water limestones of Recent, Miocene, and Eocene ages. This is an extremely interesting result showing that subsidence was continuous for a very long time, but of course nothing is learned about the composition of the ocean floor other than that during or before the Eocene there was a volcanic episode. In describing the results (H. S. Ladd *et al.*, *Bull. A. A. P. G.*, Vol. 37, 1953) the volcanic rock is referred to a 'basement rock' but this term is quite misleading as only 14 feet of basalt was penetrated and there is no evidence on its total thickness or on what may underlie it."

Notwithstanding undeniable proofs of land sinkings and the geological argument advanced by Lees in his papers partly quoted above, American scientists seem to adhere to the permanence of oceans and to other ideas opposed by Lees. Is it possible that even Lees has been forgotten, and so soon? In the most recent paper on the present subject, viz. E. L. Hamilton, *The Last Geographic Frontier: the Sea Floor*, *Scientific Monthly*, 85, 6, Dec. 1957, his name is not to be found



in the list of references. Certainly, this fact is the reason why one reads on p. 296: "The thickness of unconsolidated sediments on the ocean floor is much less than was anticipated in view of the probable great age and permanence of the main ocean basins. Why this is so is an unsolved problem at the present time." I am more inclined, however, to think that this fact is in disfavour of the permanence and corroborates the opinions of sunken land areas expressed by the many geologists and biogeographers quoted in the above pages.

Hamilton reproduces (after Menard 1955) in his just cited paper as fig. 3 an interesting area of ocean bottoms which has caused much perplexity and pondering without, however, giving rise to any acceptable explanation of its origin. This region of the bottom extends off the west coast of North America and exhibits peculiar linear fracture zones, four in number and at about equal distances running in W-E direction. Menard, in his careful inquiry into "Deformation of the Northeastern Pacific Basin and the West Coast of North America, Bull. Geol. Soc. America, 66, pp. 1149-1198, has discussed the origin of the fractures in question, and his points of view on the problem are summed up in 14 tentative conclusions without making a decision of the most probable one; he only says, on page 1173 that "the simplest hypothesis may be preferred on philosophical grounds". It seems to me that these West Pacific transverse fracture zones remind one somewhat of the transverse fissures in Greenland and Norway nowadays forming fjord valleys, and that their origin thus could be explained in the same way and simplest as due to a tension in the earth's crust perpendicular to their direction, a tension caused by an *upheaval of the bottom*, a possibility that has not been taken into consideration by Menard. However, Menard concludes (p. 1192) "a late Mesozoic or early Tertiary age for the formation of the fracture zones", a dating in agreement with the simultaneous building of the great mountain chains, which presuppose the existence of geosyncline formations, and these in turn geanticlines on their sides. The simple way out of the difficulties in explaining the fractures in question should be by means of a previous upheaval due to thermal dilatation in this region, which was later on definitely submerged by means of thermal constriction. This is in reality a well-founded geological demand of many scientists, as shown in the preceding (p. 9) as a counterpart to the orogen. Indeed, it realizes most persuasively the postulation of Born (1933, p. 393, cf. Odhner 1944, p. 38): the former land of *Cascadia*.

Tryckt den 14 april 1958

Uppsala 1958. Almqvist & Wiksells Boktryckeri AB



## Amphitalite a mixture

BY ÅKE HENRIQUES

Amphitalite was discovered at Hållsjöberget (Horrsjöberget), Värmland, Sweden, by L. J. Igelström in 1866.

Igelström (1866, I) gave the following description of the mineral (translated from the Swedish):

“With this name from the Greek, ἀμφιθαλής, beflowered on all sides, I designated a white, hydrous aluminium phosphate from the place mentioned, which occurs massive, filling cavities and veins (up to 1 inch in diameter and width). It is intergrown with and surrounded by the previously known beautiful minerals of this rock, lazulite, rutile, cyanite etc. The name refers to the earlier mentioned beautiful variegated surroundings in which the mineral is located, although it has a plain appearance itself.

Its colour is milky white, also its powder. Thin splinters are translucent, there is no distinct cleavage and the fracture is uneven.  $H = 6$ , the same as lazulite, with which the mineral is admixed or surrounded by.”

A microscopic examination of the original material in the possession of the Swedish Museum of Natural History (R. M. 060294) showed that amphitalite is a mixture of several minerals. Augelite dominates amongst these. Further various quantities of apatite, lazulite and other phosphates, rutile, quartz, kyanite, mica and an epidote mineral occur.

A powder photograph taken at the Swedish Museum of Natural History also shows that the amphitalite is mainly composed of augelite (no other minerals were established with certainty by this way, the reason being their low contents).

### REFERENCES

- IGELSTRÖM, L. J. (1866, I), Nya mineralier från Wermland, 2. Amfithalit från Horrsjöberget i Nysocken, Elfdals härad. Wermland. Ak. Stockholm, Handl. Öfv., 23, 95–96.  
 — (1866, II), Die Mineralien von Horrsjöberg in Wermland; Amphitälit, Svanbergit, Damourit, Pyrophyllit, Kyanit, Lazulit, Rutil u. s. w. B. H. Ztg., 25, 309.

Tryckt den 8 augusti 1958

Uppsala 1958. Almqvist & Wiksells Boktryckeri AB





# Tetragophosphite discredited

By ÅKE HENRIQUES

Tetragophosphite was discovered at Hållsjöberget (Horrsjöberget), Värmland, Sweden by L. J. Igelström in 1896.

Igelström (1896) gave the following description of the mineral:

„ . . . Der Tetragophosphit findet sich auf Spalten und Rissen eines aus Cyanit und Damourit bestehenden Gesteines in vierseitigen Kristalltafeln von 2–3 mm Dicke und 20–30 mm Länge,

Table 1. Minerals from Hållsjöberget first named and described by L. J. Igelström.

Igelström's name	Actual identity
Empholite <sup>1</sup>	Diaspore <sup>2</sup>
Talktriplite <sup>3</sup>	Wagnerite <sup>4</sup>
Amphitalite <sup>5</sup>	Augelite <sup>6</sup>
Rhodophosphite <sup>7</sup>	Manganoan Apatite 8*
Tetragophosphite <sup>7</sup>	Lazulite <sup>9</sup>
Svanbergite <sup>10</sup>	Svanbergite <sup>11</sup>

<sup>1</sup> IGELSTRÖM, L. J. (1883), Emfolit, ett nytt mineral från Horrsjöberg i Vermland. Kungl. Vet. Akad. Stockholm, Öfv., 40, 7, 97–102.

<sup>2</sup> NORDENSKIÖLD, A. E. (1887), Mineralogiska bidrag, Diaspor från Horrsjöberget i Vermland. Geol. Förh. 9, 30–34.

<sup>3</sup> IGELSTRÖM, L. J. (1882), Nya mineral från Vermland, Talktriplit, ett nytt mineral från Horrsjöberg i Wermland. Kungl. Vet. Akad. Stockholm, Öfv., 39, 86–91.

<sup>4</sup> HENRIQUES, Å. (1956), An iron-rich wagnerite, formerly named talktriplite, from Hållsjöberget (Horrsjöberget), Sweden. Arkiv f. Mineralogi och geologi 2, 149–153.

<sup>5</sup> IGELSTRÖM, L. J. (1866), Nya mineralier från Wermland, Amfithalit från Horrsjöberget i Ny socken, Elfdals härad, Wermland. Kungl. Vet. Akad. Stockholm, Öfv., 23, 95–96.

<sup>6</sup> HENRIQUES, Å. (1958), The identity of amphitalite. Arkiv f. Mineralogi och geologi. In press.

<sup>7</sup> IGELSTRÖM, L. J. (1896), Rhodophosphit und Tetragophosphit, zwei neue Mineralien von Horrsjöberg in Wermland. Zs. Kr. 25, 433–435.

<sup>8</sup> HINTZE (1933), Handbuch der Mineralogie, vol. 4, pt. 1, 620. Klockmann-Ramdohr (1936), Lehrbuch der Mineralogie, 11. Aufl. Stuttgart.

<sup>9</sup> This paper.

<sup>10</sup> IGELSTRÖM L. J. (1854), Nya svenska mineralier. Kungl. Vet. Akad. Stockholm, Öfv., 11, 156–159.

<sup>11</sup> YGBERG, E. R. (1945), Svanbergite from Horrsjöberg. Ark. Kemi 20 A, n:o 4, 1–17.

\* Ramdohr (1936) has suggested from the description of the mineral (Hintze, 1933) that rhodophosphite must be a manganoan apatite. A powder photograph of the original material (No. g 28021) in the collection of the Swedish Museum of Natural History also shows that rhodophosphite is identical with apatite.

aber auch in dünnen unregelmässigen Überzügen und Häutchen. Er ist offenbar eine spätere Bildung und durch Infiltration in die Gesteinsspalten gelangt.

Der Tetragophosphit gleicht dem Lazulith und ist ein sehr schön blaues, durchsichtiges, homogenes Mineral. Der Farbenton ist aber etwas heller wie der des Lazuliths.“

The microscopic examination of the original material (No. g 32461) in the collection of the Swedish Museum of the Natural History disclosed that tetragophosphite is a recrystallized lazulite (probably poor in iron and manganese).

A powder photograph also shows that tetragophosphite is identical with lazulite.

This investigation concludes the examination of the minerals named by L. J. Igelström from the kyanite-quartzite from Hållsjöberget. Table 1 indicates that svanbergite is the only really new mineral of the deposit.

#### REFERENCE

HINTZE (1933), Handbuch der Mineralogie, vol. 4, pt. 1, 620.

IGELSTRÖM, L. J. (1896), Rhodophosphit und Tetragophosphit, zwei neue Mineralien von Horrsjöberg in Wermland. Zs. Kr. 25, 433–435.

KLOCKMANN-RAMDOHR (1936), Lehrbuch der Mineralogie, 11. Aufl. Stuttgart.

Tryckt den 8 augusti 1958

Uppsala 1958. Almqvist & Wiksells Boktryckeri AB

## Notes on the mineralogy of Sweden. 1-2

By ERIC WELIN<sup>1</sup>

### 1. Andersonite, liebigite and schroeckingerite from Stripa, Västmanland

In the winter of 1957 fluorescent uranium minerals were for the first time observed in the Stripa iron mine. This mine works a quartz-banded iron ore which has been described by Geijer (1938). The chief constituents of the ore are hematite, quartz and skarn silicates. Magnetite usually occurs as scattered porphyroblastic grains in the hematite bands. The deposit consists of two superimposed synclinally folded layers in a wide area of Archean leptites. These are intruded by some few small amphibolite dikes and finally by granite and dikes of granite aplite. Of these intrusions, at least the granite and the granite aplite are younger than the folding of the leptite-ore complex and the concluding faulting. The only feature Geijer has found to be of post-Archean age is a system of numerous faults, which generally show no great displacement.

In 1956 uranium-bearing fissure fillings were observed in the mine. They are best developed in the upper main ore body but they also exist in the lower ore body, and to some extent also in the leptite and in the granite. The investigation of this uranium mineralization is still in progress and the results will be published later. The secondary uranium minerals have been found in connection with the black uranium fissures as a thin coating in small cracks and on the walls of the drifts. They have been identified as andersonite,  $\text{Na}_2\text{Ca}(\text{UO}_2)(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$ , liebigite,  $\text{Ca}_2(\text{UO}_2)(\text{CO}_3)_3 \cdot 10\text{H}_2\text{O}$ , and schroeckingerite,  $\text{NaCa}_3(\text{UO}_2)(\text{CO}_3)_3(\text{SO}_4)\text{F} \cdot 10\text{H}_2\text{O}$ , by means of X-ray powder photographs. These were made on a Philips Debye-Scherrer camera with a diameter of 114.83 using filtered Cu radiation. The intensities were estimated visually. In Tables 1-3 the measured spacings are compared with published values.

Andersonite has so far only been identified in one place in the mine as crystals coating an area of some square centimeters on a drift wall. The grassgreen, rhombohedral crystals of andersonite are about one millimeter in diameter and show a pseudocubic habit. One of the crystals showed a well developed terminal face. On this crystal  $\omega = 1.524$  could be determined. The specific gravity of andersonite is 2.80 and the fluorescence, bright green. Andersonite was first described by Axelrod *et al.* (1951) who found the specific gravity to be 2.80 and  $\omega = 1.520$ .

The color of liebigite, being very similar to that of andersonite, makes it impossible to distinguish between the two minerals megascopically if crystal faces are not developed. This has been the case only in the above mentioned occurrence

<sup>1</sup> AB Atomenergi, Stockholm.

Table 1. Interplanar spacings from X-ray powder patterns.

Andersonite, Stripa		Andersonite, Arizona Axelrod <i>et al.</i> (1951)		Andersonite, Stripa		Andersonite, Arizona Axelrod <i>et al.</i> (1951)	
$d_{\text{obs}}$ Å	$I$	$d_{\text{obs}}$ Å	$I$	$d_{\text{obs}}$ Å	$I$	$d_{\text{obs}}$ Å	$I$
12.73	3	13.0	10	1.932	1	1.933	1
9.46	3	9.51	3	1.894	1	1.895	4
7.94	9	7.97	10	1.846	3	1.852	6
6.54	2	6.56	2	1.812	1		
5.72	9	5.68	10	1.775	1		
5.24	10	5.22	10	1.747	1	1.749	1
4.33	7	4.35	6	1.732	1		
4.19	7	4.19	6	1.679	1	1.684	3
4.05	6	4.04	4	1.654	1		
3.83	1	3.82	3	1.629	1		
3.69	8	3.71	8	1.603	1		
3.49	1	3.49	2	1.571	2	1.573	4
3.33	1	3.34	2	1.546	1		
3.15	3	3.15	5 b	1.522	1		
3.00	6	3.00	7	1.503	1		
2.85	0.5			1.466	1		
2.798	5	2.79	6	1.441	1		
2.643	1			1.408	1		
2.450	3	2.45	5	1.390	1	1.393	3
2.383	2	2.36	4	1.347	1	1.344	3
2.352	2			1.313	1		
2.203	5	2.21	7	1.275	1		
2.115	1			1.259	1	1.262	3
2.032	1	2.04	4	1.245	1		
2.007	1	2.01	4	1.230	0.5	1.232	3
1.974	1	1.977	4	1.194	0.5		
1.953	1	1.957	4	1.175	0.5		

of andersonite. The fluorescence of liebigite is also very similar to that of andersonite. The measured specific gravity of liebigite is 2.41, which is the same as Evans and Frondel (1950) found on a specimen from Joachimsthal, Bohemia.

The appearance of schroeckingerite is quite different from andersonite and liebigite. It forms wartlike, earthy masses of yellow-white color and at most one millimeter in diameter. In the handspecimen containing the previously mentioned andersonite, some of these crystals are covered with small schroeckingerite warts. The fluorescence of the Stripa schroeckingerite is bright whitish green and not, as described by Axelrod *et al.*, similar to that of andersonite. The specific gravity is 2.54. On specimens from Argentina, Utah and Wyoming, Hurlbut determined the specific gravity to be 2.550, 2.544 and 2.5.

As already described, the minerals appear both in small cracks in the rock and in the ore and also on the walls of the drifts. The minerals on the walls, at least, must have been formed after the mining operation, and must accordingly be very young. It has in fact been established that after a time of 1-2 months the walls of new drifts fluoresce strongly. In order to investigate the conditions during which the minerals are precipitated from the aqueous solutions, an analysis has been performed on water from the mine. (Table 4.)

This analysis, made by the Analytical Section of AB Atomenergi, shows a



Table 2. Interplanar spacings from X-ray powder patterns.

Liebigite, Stripa		Liebigite, Joachimstal USGS Bull. 1036-G		Liebigite, Joachimstal Evans and Frondel (1950)	
$d_{\text{obs}}$ Å	$I$	$d_{\text{obs}}$ Å	$I$	$d_{\text{obs}}$ Å	$I$
8.86	9	8.68	9		
8.28	7	8.27	1		
7.52	0.5				
6.82	10	6.81	10	6.81	9
6.08	1	6.11	2	6.07	2
5.52	10	5.40	9	5.37	10
4.95	0.5	4.95	1	4.98	1
4.55	8	4.55	6	4.55	6
4.21	0.5				
4.18	0.5	4.17	1		
4.06	3	4.04	2	4.10	5
3.93	1	3.95	1	3.93	1
3.78	1	3.75	2	3.79	2
3.58	2	3.58	3	3.60	4
3.32	2	3.33	5	3.35	7
		3.31	5		
3.20	1	3.19	1		
3.11	9	3.10	6	3.16	8
3.05	1	3.02	1	3.04	2
2.99	1				
2.834	1	2.84	1	2.85	2
2.761	1	2.77	1	2.78	2
2.665	1	2.66	1	2.71	1
2.591	1	2.57	3	2.59	4
2.549	1				
2.437	1	2.44	1	2.47	3
		2.37	2		
2.305	1	2.30	2	2.32	3
2.257	1	2.26	2	2.28	3
2.143	1	2.15	4	2.18	4
2.101	2	2.10	1	2.12	2
2.066	1			2.05	1
2.030	0.5	2.02	1		
1.987	3	1.998	5	2.01	5
1.956	1	1.957	1		
1.909	1	1.911	1	1.929	2
1.880	1	1.884	1		
1.837	1	1.830	1	1.852	1
1.714	2	1.716	5	1.731	4
1.665	1	1.670	3	1.684	2
1.617	0.5			1.631	1
1.559	1	1.561	2	1.575	2
1.532	0.5	1.533	1	1.547	1
1.483	0.5	1.484	1	1.497	1
1.461	0.5	1.473	2	1.473	2
1.431	0.5	1.437	1	1.451	1
1.411	0.5	1.416	1	1.423	1
1.395	0.5	1.397	1	1.402	1
1.344	0.5	1.347	2	1.358	2
1.341	0.5				
				1.329	1
1.293	0.5			1.301	2
1.272	0.5			1.285	2
1.245	0.5			1.258	2
1.211	0.5			1.222	2
1.177	0.5			1.182	1
1.134	0.5			1.167	1
1.125	0.5				
1.074	0.5				

Table 3. Interplanar spacings from X-ray powder patterns.

Schroëckingerite, Stripa		Schroëckingerite, Wyoming Jaffe <i>et al.</i> (1948)	
$d_{\text{obs}}$	$I$	$d_{\text{obs}}$	$I$
14.75	0.5	14.5	5
8.33	4	8.3	4+
7.19	10	7.2	10
5.55	5	5.62	1+
5.36	5	5.45	1+
		5.32	1
4.80	8	4.81	6
		4.26	1
4.15	4	4.18	1+
4.03	4	4.06	1
		3.61	1
3.34	1	3.37	1
		3.32	1
		3.24	1
3.12	1 b	3.1	1 b
2.874	3	2.88	6
2.772	3	2.78	1
2.696	0.5	2.71	1
2.621	0.5	2.63	1
2.392	2	2.40	1+
2.297	2	2.30	1 b
2.115	1	2.12	1
2.046	1	2.05	3
1.906	2		
1.816	2		
1.789	1	1.80	1+
1.664	0.5		
1.568	0.5		
1.331	0.5		

deficit of uranium with respect to the other components of minerals. Therefore the total amount of uranyl carbonates which crystallize from the aqueous solutions depends only on the uranium content. The amount of each uranyl carbonate is, however, unknown.

The solubility of schroëckingerite is 4.02 g/l at pH 6.0 (22°C) (Ross 1955) and, as andersonite in one specimen is covered by schroëckingerite, its solubility most probably is lower than that of schroëckingerite. By dissolving liebigite in distilled water with a pH of 6.0, a saturation was found at 4.22 g/l (20°C). This determination shows that liebigite is slightly more soluble than schroëckingerite (and andersonite). Lack of material made it impossible to carry out a determination of the solubility of andersonite.

If the order of crystallization was regulated by the solubility of the minerals only one of the carbonates would form. This is not the case, and other factors than the solubility therefore may influence the order of crystallization as e.g. different composition of the water, or variable humidity of the air.

A contributive circumstance to the precipitation of the uranyl carbonates is the high pH value 8.1 of the water, since Ross has shown in the synthesis of

Table 4. Chemical analysis of water from Stripa iron mine.

	mg/l
Consumption of $\text{KMnO}_4$ . . . . .	6
Residue of evaporation . . . . .	226
Residue of evaporation, ignited $600^\circ \text{C}$ . . . . .	159
U . . . . .	2.4
Ca . . . . .	40.7
Mg . . . . .	3.6
Na . . . . .	20.9
K . . . . .	2.3
Fe . . . . .	0.15
$\text{HCO}_3$ . . . . .	130
$\text{SO}_4$ . . . . .	27
$\text{PO}_4$ . . . . .	< 1
$\text{CO}_2$ , free . . . . .	2.4
$\text{H}_2\text{S}$ . . . . .	< 1
F . . . . .	not determined

schroëckingerite that the solubility of this mineral probably approaches a minimum at pH 9. The synthesis of andersonite also has been carried out at pH 8–9 (Axelrod *et al.*). The temperature in the mine is  $+5$  to  $+8^\circ \text{C}$  and the relative humidity in the central part of the mine is 90 % during the summer and nearly 100 % during the winter (Larsson 1956). Since the solubility of schroëckingerite at this temperature and at pH 8.0 can be estimated to be roughly 1.5 g/l, and since, at most, 8.95 mg/l schroëckingerite can be formed from the total uranium content of the water (2.4 m/l), a practically complete evaporation of the water is necessary for precipitation. This is possible on the walls and roofs of the drifts, which have an extensive, thin water cover, and which are passed by ventilation air at the rate of 6–10 m<sup>3</sup>/sec. In all, 128 m<sup>3</sup>/sec. air with an average relative humidity of 80 % is supplied continuously to the mine. The excess  $\text{CO}_2$  in the water, which may influence the solubility of the uranyl carbonates, also has the greatest possibility to evaporate when the water is spread out over the walls.

## ACKNOWLEDGMENT

The writer wishes to acknowledge his indebtedness to Stållbergs Gruive AB and AB Atomenergi for permission to publish this paper.

## REFERENCES

- AXELROD, J. M., GRIMALDI, F. S., MILTON, C., and MURATA, K. J. (1951), American Mineralogist 36, 1.  
 EVANS, H. T. JR., and FRONDEL, C. (1950), American Mineralogist 35, 251.  
 GEIJER, P. (1938), Sveriges Geologiska Undersökning. Ser. Ca, No 28.  
 HURLBUT, C. S., JR. (1954), American Mineralogist 39, 901.  
 JAFFE, H. W., SHERWOOD, A. M., and PETERSON, M. J. (1948), American Mineralogist 33, 152.  
 LARSSON, ORVAR (1956), Teknisk Tidskrift 86, 341.  
 U. S. Geologiska Survey Bull. 1036-G (1956).

## 2. Ferrocolumbite from Sörhällan, Norrbotten

This mineral was found in the Sörhällan feldspar quarry, south of Råneå, during the course of mapping in the Norrbotten county by the Geological Survey. The quarry is, according to Sundius (1951), situated on the hanging wall side of a graphic-granite vein, which consists mainly of reddish feldspar and quartz with some dark or light-coloured mica, tourmaline, garnet and beryl. The ferrocolumbite occurs as black irregular masses between feldspar crystals in the available small samples, borrowed from the Swedish Museum of Natural History (RMA 51 0324-51 0326). It is partly covered by a thin yellow incrustation which also occurs in the cavities and cracks of the ferrocolumbite. The yellow mineral is usually earthy but may locally change to a glassy translucent mass.

The ferrocolumbite was identified by means of X-ray powder photographs. In Table 1 the measured  $d$ -spacings are compared with the values of a columbite from Mitchell Co., N.C., published by Berman (1955). The X-ray powder data were measured on a Philips Debye-Scherrer camera with a radius of 57.3 mm using filtered Cu radiation. The intensities were estimated visually.

A chemical analysis of the ferrocolumbite has been performed by Miss Th. Berggren. The result of this analysis is shown in Table. 2.

The molecular quotients are, if the water is assumed to be hygroscopic

$$AO : B_2O_5 = 1.00 : 1.02$$

Table 1. Interplanar spacings from X-ray powder patterns.

Ferrocolumbite, Råneå		Columbite, Mitchell Co., N.C.	
$d_{\text{obs}}$ Å	$I$	$d_{\text{obs}}$ Å	$I$
		7.15	1
3.65	6	3.65	4
2.97	10	2.97	10
		2.87	2
		2.55	1
2.52	2 b	2.50	2
2.371	1	2.38	1
2.214	1	2.21	1.5
2.092	2	2.09	1
1.907	1	1.91	2
1.830	1	1.83	1 b
1.770	1	1.77	1 b
		1.74	2 b
1.725	4	1.72	3 b
1.541	2	1.542	2 b
1.457	3	1.464	3 b
1.382	1	1.380	1
1.312	0.5		
1.238	0.5		
1.216	0.5		
1.192	1		
1.098	1		



Table 2. Chemical composition of ferrocolumbite, Råneå.

	Weight %	Molecular ratios	
H <sub>2</sub> O	1.6	0.0889	0.0889
Na <sub>2</sub> O	0.3	0.0048	
MgO	0.8	0.0198	
CaO	0.6	0.0107	
MnO	2.9	0.0409	
FeO	14.6	0.2032	4O 0.2829
Ce <sub>2</sub> O <sub>3</sub> / & c.	0.5	0.0029	
U <sub>3</sub> O <sub>8</sub>	0.2	0.0002	
ThO <sub>2</sub>	0.1	0.0004	
TiO <sub>2</sub>	1.1	0.0138	
Nb <sub>2</sub> O <sub>5</sub>	68.7	0.2584	B <sub>2</sub> O <sub>5</sub> 0.2896
Ta <sub>2</sub> O <sub>5</sub>	7.7	1.0174	
Total	99.1		

Accordingly, the formula of the mineral can be written



where X = small quantities of Mg, Ca, Na, Ce, U and Th.

From the Ta content the specific gravity can be calculated to be  $5.43 \pm 0.05$  (Palache *et al.*). The measured value of the specific gravity is  $5.26 \pm 0.05$ .

The radioactive yellow incrustations in the fissures and on the surface of the ferrocolumbite only shows a very weak powder line with a *d*-spacing of 3.32 Å. It does not fluoresce when illuminated with UV light. Other physical or chemical determinations have not been possible to carry out on account of the small available amounts of the mineral. As the ferrocolumbite contains some uranium it is obvious that the yellow incrustations consists of a supergene uranium mineral.

#### REFERENCES

- BERMAN, J. (1955), *American Mineralogist* 40, 805.  
 PALACHE, C., BERMAN H., and FRONDEL, C. (1944), *Dana's System of Mineralogy*, Vol. I, p. 786.  
 SUNDIUS, N. (1951), *Sveriges Geologiska Undersökning*, Ser. C. No 520.

Tryckt den 8 augusti 1958

Uppsala 1958. Almqvist & Wiksells Boktryckeri AB



# The influence of cations on the optical properties of clinopyroxenes

## Part II

By ÅKE HENRIQUES

### SUMMARY

Regression equations of the second degree for the optical properties ( $\alpha$ ,  $\beta$ ,  $\gamma$  and  $2V$ ) as a function of the chemical composition of clinopyroxenes have been calculated.

In part I (Henriques, 1958) the connexion between chemical composition and optical properties ( $\alpha$ ,  $\beta$ ,  $\gamma$  and  $2V$ ) for clinopyroxenes was derived with regression equations of the type:

$$\alpha = a_{\alpha} + \sum a_{i\alpha} N_i, \quad (1)$$

$$\beta = a_{\beta} + \sum a_{i\beta} N_i, \quad (2)$$

$$\gamma = a_{\gamma} + \sum a_{i\gamma} N_i, \quad (3)$$

$$2V = a_{2V} + \sum a_{i2V} N_i, \quad (4)$$

where  $a_{\alpha}$ ,  $a_{\beta}$ ,  $a_{\gamma}$  and  $a_{2V}$  are constants,  $a_{i\alpha}$ ,  $a_{i\beta}$ ,  $a_{i\gamma}$  and  $a_{i2V}$  represent the effects of the cation of type  $i$  on the refractive indices  $\alpha$ ,  $\beta$ ,  $\gamma$ , and the optic axial angle  $2V$ .  $N$  is the number of the cations in a fixed volume.

The author has also shown earlier (Henriques, 1957):

“The partial regression equations possess solely descriptive character and rely entirely on the assumption that the optical properties are additively composed of and are linear functions of the relative contents of the elements. This should be the case, at least approximately, within a mineral group showing substitution solid solution and whose properties vary continuously with the composition. Now, polarization effects and other lattice effects are able to influence the optical properties to some extent so that these deviate from the strictly linear function. As a result hereof full agreement between the determined and calculated values cannot be obtained. Better agreement between reckoned and observed values is obtained by using equations of the form:

$$\alpha = a_{\alpha} + \sum a_{i\alpha} N_i + \sum a'_{i\alpha} N_i^2, \quad (5)$$

$$\beta = a_{\beta} + \sum a_{i\beta} N_i + \sum a'_{i\beta} N_i^2, \quad (6)$$

$$\gamma = a_{\gamma} + \sum a_{i\gamma} N_i + \sum a'_{i\gamma} N_i^2, \quad (7)$$

$$2V = a_{2V} + \sum a_{i2V} N_i + \sum a'_{i2V} N_i^2. \quad (8)$$

By differentiating the equations devised by Hori and the author (here only carried out for  $\alpha$ ) one obtains:

$$d\alpha = \sum a_{i\alpha} dN_i, \quad (9)$$

$$d\alpha = \sum a_{i\alpha} dN_i + 2 \sum a'_{i\alpha} N_i dN_i. \quad (10)$$

Optical properties for clinopyroxenes according to equations of type (5)–(8).<sup>1</sup>

$$\begin{aligned} \alpha = & (1.862 \pm 1.520) \text{ Si} - (0.515 \pm 0.580) \text{ Si}^2 - (0.105 \pm 0.588) \text{ Al} + \\ & (0.283 \pm 0.272) \text{ Al}^2 - (0.507 \pm 0.948) \text{ Ti} + (9.591 \pm 6.314) \text{ Ti}^2 + \\ & (0.527 \pm 0.415) \text{ Cr} - (14.849 \pm 10.482) \text{ Cr}^2 - (0.059 \pm 0.570) \text{ Fe}^{3+} + \\ & (0.744 \pm 0.397) \text{ Fe}^{3+2} + (0.070 \pm 0.348) \text{ Fe}^{2+} - (0.036 \pm 2.655) \text{ Fe}^{2+2} + \\ & (0.164 \pm 0.324) \text{ Mn} - (1.258 \pm 1.053) \text{ Mn}^2 - (0.035 \pm 0.369) \text{ Mg} + \\ & (0.008 \pm 2.209) \text{ Mg}^2 + (0.091 \pm 0.385) \text{ Ca} - (0.063 \pm 0.086) \text{ Ca}^2 - \\ & (0.112 \pm 0.219) \text{ Na} + (0.901 \pm 0.797) \text{ Na}^2 - (0.230 \pm 0.438) \text{ K} + \\ & (42.400 \pm 45.890) \text{ K}^2. \end{aligned} \quad (11)$$

$$\begin{aligned} \beta = & (2.266 \pm 1.520) \text{ Si} - (0.668 \pm 0.580) \text{ Si}^2 - (0.261 \pm 0.588) \text{ Al} + \\ & (0.338 \pm 0.272) \text{ Al}^2 - (0.840 \pm 0.948) \text{ Ti} + (12.369 \pm 6.314) \text{ Ti}^2 + \\ & (0.356 \pm 0.415) \text{ Cr} - (14.783 \pm 10.481) \text{ Cr}^2 - (0.214 \pm 0.570) \text{ Fe}^{3+} + \\ & (0.940 \pm 0.397) \text{ Fe}^{3+2} - (0.032 \pm 0.348) \text{ Fe}^{2+} - (0.032 \pm 0.027) \text{ Fe}^{2+2} + \\ & (0.066 \pm 0.324) \text{ Mn} - (1.278 \pm 1.053) \text{ Mn}^2 - (0.138 \pm 0.369) \text{ Mg} + \\ & (0.011 \pm 0.022) \text{ Mg}^2 + (0.015 \pm 0.385) \text{ Ca} - (0.076 \pm 0.086) \text{ Ca}^2 - \\ & (0.133 \pm 0.219) \text{ Na} + (0.665 \pm 0.797) \text{ Na}^2 - (0.416 \pm 0.438) \text{ K} + \\ & (56.055 \pm 45.887) \text{ K}^2. \end{aligned} \quad (12)$$

$$\begin{aligned} \gamma = & (2.559 \pm 1.675) \text{ Si} - (0.775 \pm 0.639) \text{ Si}^2 - (0.377 \pm 0.648) \text{ Al} + \\ & (0.405 \pm 0.300) \text{ Al}^2 - (0.866 \pm 1.044) \text{ Ti} + (11.054 \pm 6.957) \text{ Ti}^2 + \\ & (0.362 \pm 0.458) \text{ Cr} - (18.435 \pm 11.549) \text{ Cr}^2 - (0.323 \pm 0.628) \text{ Fe}^{3+} + \\ & (0.958 \pm 0.437) \text{ Fe}^{3+2} - (0.097 \pm 0.384) \text{ Fe}^{2+} - (0.027 \pm 0.029) \text{ Fe}^{2+2} - \\ & (0.013 \pm 0.357) \text{ Mn} - (1.201 \pm 1.160) \text{ Mn}^2 - (0.191 \pm 0.407) \text{ Mg} + \\ & (0.005 \pm 0.024) \text{ Mg}^2 - (0.068 \pm 0.425) \text{ Ca} - (0.066 \pm 0.094) \text{ Ca}^2 - \\ & (0.176 \pm 0.241) \text{ Na} + (0.610 \pm 0.878) \text{ Na}^2 - (0.439 \pm 0.483) \text{ K} + \\ & (60.134 \pm 50.564) \text{ K}^2. \end{aligned} \quad (13)$$

$$\begin{aligned} 2V = & (278.63 \pm 2087.85) \text{ Si} - (115.32 \pm 796.57) \text{ Si}^2 - (66.84 \pm 807.92) \text{ Al} - \\ & (20.69 \pm 373.37) \text{ Al}^2 - (750.68 \pm 1301.35) \text{ Ti} + (6444.52 \pm 8671.20) \text{ Ti}^2 + \\ & (16.51 \pm 570.35) \text{ Cr} - (9997.82 \pm 14394.25) \text{ Cr}^2 - (151.98 \pm 782.79) \text{ Fe}^{3+} + \\ & (491.03 \pm 544.89) \text{ Fe}^{3+2} - (91.16 \pm 478.43) \text{ Fe}^{2+} + (44.09 \pm 36.45) \text{ Fe}^{2+2} - \\ & (385.46 \pm 444.96) \text{ Mn} + (2130.24 \pm 1446.02) \text{ Mn}^2 - (76.69 \pm 507.30) \text{ Mg} + \\ & (7.49 \pm 30.33) \text{ Mg}^2 + (147.30 \pm 529.12) \text{ Ca} - (115.24 \pm 117.48) \text{ Ca}^2 + \\ & (70.04 \pm 300.27) \text{ Na} - (143.31 \pm 1094.04) \text{ Na}^2 - (404.87 \pm 601.93) \text{ K} - \\ & (9886.86 \pm 63018.51) \text{ K}^2. \end{aligned} \quad (14)$$

<sup>1</sup> Si, Al, Ti . . . is the number of  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ti}^{4+}$  ions . . . based on  $6\text{O}^{-2}$ .



Table 1. Calculated and observed refractive indices of clinopyroxenes according to equations (11)–(13).

No.	$\alpha_{\text{calc}}$	$\alpha_{\text{obs}}$	$\Delta\alpha$	$\beta_{\text{calc}}$	$\beta_{\text{obs}}$	$\Delta\beta$	$\gamma_{\text{calc}}$	$\gamma_{\text{obs}}$	$\Delta\gamma$
1	1.672	1.672	0.000	1.679	1.678	−0.001	1.701	1.701	0.000
2	1.674	1.674	0.000	1.680	1.680	0.000	1.702	1.702	0.000
3	1.680	1.680	0.000	1.685	1.684	−0.001	1.705	1.706	0.001
4	1.681	1.681	0.000	1.686	1.685	−0.001	1.707	1.706	−0.001
5	1.680	1.681	0.001	1.684	1.685	0.001	1.705	1.708	0.003
6	1.682	1.682	0.000	1.687	1.687	0.000	1.709	1.709	0.000
7	1.683	1.683	0.000	1.687	1.686	−0.001	1.710	1.709	−0.001
8	1.679	1.682	0.003	1.684	1.687	0.003	1.707	1.709	0.002
9	1.683	1.682	−0.001	1.688	1.688	0.000	1.711	1.710	−0.001
10	1.683	1.683	0.000	1.688	1.687	−0.001	1.711	1.710	−0.001
11	1.687	1.687	0.000	1.692	1.692	0.000	1.715	1.715	0.000
12	1.693	1.691	−0.002	1.698	1.695	−0.003	1.720	1.719	−0.001
13	1.692	1.692	0.000	1.698	1.697	−0.001	1.720	1.719	−0.001
14	1.698	1.699	0.001	1.704	1.706	0.002	1.725	1.727	0.002
15	1.699	1.700	0.001	1.707	1.706	−0.001	1.728	1.728	0.000
16	1.708	1.708	0.000	1.714	1.714	0.000	1.736	1.736	0.000
17	1.708	1.708	0.000	1.714	1.715	0.001	1.735	1.735	0.000
18	1.722	1.723	0.001	1.730	1.730	0.000	1.750	1.751	0.001
19	1.735	1.736	0.001	1.745	1.745	0.000	1.764	1.763	0.001
20	1.697	1.698	0.001	1.706	1.706	0.000	1.724	1.724	0.000
21	1.691	1.689	−0.002	1.697	1.695	−0.002	1.718	1.716	−0.002
22	1.693	1.693	0.000	1.698	1.698	0.000	1.720	1.720	0.000
23	1.701	1.699	−0.002	1.706	1.705	−0.001	1.727	1.726	−0.001
24	1.707	1.709	0.002	1.713	1.714	0.001	1.733	1.734	0.001
25	1.716	1.715	−0.001	1.721	1.721	0.000	1.740	1.740	0.000
26	1.711	1.710	−0.001	1.717	1.715	−0.002	1.737	1.735	−0.002
27	1.726	1.726	0.000	1.733	1.733	0.000	1.755	1.755	0.000
28	1.691	1.693	0.002	1.695	1.697	0.002	1.718	1.722	0.004
29	1.694	1.694	0.000	1.698	1.698	0.000	1.722	1.722	0.000
30	1.693	1.694	0.001	1.698	1.698	0.000	1.721	1.722	0.001
31	1.695	1.695	0.000	1.699	1.701	0.002	1.723	1.725	0.002
33	1.697	1.697	0.000	1.701	1.701	0.000	1.725	1.724	−0.001
35	1.674	1.672	−0.002	1.679	1.679	0.000	1.702	1.701	−0.001
36	1.675	1.674	−0.001	1.680	1.681	0.001	1.702	1.703	0.001
37	1.602	1.692	0.000	1.699	1.698	−0.001	1.719	1.719	0.000
38	1.705	1.707	0.002	1.712	1.714	0.002	1.730	1.733	0.003
39	1.722	1.721	−0.001	1.730	1.729	−0.001	1.747	1.746	−0.001

From equation (9) it becomes apparent that  $d\alpha$  is a function of the changes in the chemical constitutions, while equation (10) is a function of both the chemical contents and their variations."

Regression equations for  $\alpha$ ,  $\beta$ ,  $\gamma$  and  $2V$  were calculated from the same material (Hess, 1949) as in part I.

In Tables 1 and 2 calculated and determined values for the refractive indices and for the axial angle are presented.

A table illustrating the changes in refractive indices by ionic substitution of 1 atomic per cent of an ion with another for the clinopyroxenes (Henriques, 1958), cannot be derived. As the regression equations contain terms of the second degree the optical properties will be dependent on the absolute contents of the ionic species.

Table 2. Calculated and observed optical angles of clinopyroxenes according to equation (14).

No.	$2V_{\text{calc}}$	$2V_{\text{obs}}$	$\Delta 2V$	No.	$2V_{\text{calc}}$	$2V_{\text{obs}}$	$\Delta 2V$
1	58	58	0	20	66	66	0
2	55	56	1	21	55	56	1
3	51	50	-1	22	55	55	0
4	48	49	1	23	56	56	0
5	49	49	0	24	57	56	-1
6	49	49	0	25	57	57	0
7	47	48	1	26	55	54	-1
8	52	52	0	27	59	59	0
9	52	52	0	28	46	44	-2
10	51	52	1	29	47	47	0
11	48	51	3	30	47	47	0
12	48	48	0	31	45	49	4
13	52	51	-1	33	43	40	-3
14	59	58	-1	35	55	57	2
15	52	49	-3	36	58	57	-1
16	60	60	0	37	58	59	1
17	53	57	4	38	61	62	1
18	63	63	0	39	68	68	0
19	72	70	-2				

Tables 1 and 2 and 1-4 in part I show that better agreement between observed and calculated values is obtained when regression equations with quadratic terms are employed. This would seem to be primarily due to the fact that, as already noted, the optical properties of clinopyroxenes are not strictly linear functions of the chemical composition of the mineral.

The regression equations were solved with a digital computer (BESK), (Henriques, 1958).

## REFERENCES

- HENRIQUES, Å. (1957), The effect of cations on the optical properties and the cell dimensions of knebelite and olivine. *Arkiv för Mineralogi och Geologi* 2, 17, 305-313.  
 — (1958), The influence of cations on the optical properties of clinopyroxenes. Part I. *Arkiv för Mineralogi och Geologi* 2, 22, 341-348.  
 HESS, H. H. (1949), Chemical composition and optical properties of common clinopyroxenes. Part I. *Am. Min.* 34, 621-666.  
 HORI, F. (1954), Effects of Constituents Cations on the Optical Properties of Clinopyroxenes. *Scientific Papers of the College of General Education, University of Tokyo IV*, 71-83.

Tryckt den 8 augusti 1958

Uppsala 1958. Almqvist & Wiksells Boktryckeri AB

## The influence of cations on the optical properties of orthopyroxenes

By ÅKE HENRIQUES

Hori (1954) and the author have published calculations of the optical properties of clinopyroxenes ( $\alpha$ ,  $\beta$ ,  $\gamma$  and  $2V$ ) as functions of the chemical composition. The calculations were in both cases based on material obtained from an examination of the optical and chemical properties of clinopyroxenes (Hess, 1949). The results of Hori's and the present author's calculations do not quite agree, owing to the fact that the regression equations derived for the solution of the problem differ formally somewhat from each other (Henriques, 1957).

Hori (1956) also derived corresponding equations for orthopyroxenes. In the following the present author has derived anew regression equations for the same mineral group in accordance with the method used for the clinopyroxenes.

The equations for  $\alpha$  and  $\beta$  were calculated on the basis of the same material as was used by Hori. The basis was increased for the determination of  $\gamma$ , however, with material used by Hori for control of the equations obtained. In the latter case it was found that this causes an essential reduction in errors (see equations 4–9).

The formula of orthopyroxenes indicates that two inner relationships exist (Henriques, 1957). In order to permit solution of the equation systems

$$\alpha = a_{\alpha} + \sum a_{i\alpha} N_i, \quad (1)$$

$$\beta = a_{\beta} + \sum a_{i\beta} N_i, \quad (2)$$

$$\gamma = a_{\gamma} + \sum a_{i\gamma} N_i, \quad (3)$$

where  $a_{\alpha}$ ,  $a_{\beta}$  and  $a_{\gamma}$  are constants,  $a_{i\alpha}$ ,  $a_{i\beta}$  and  $a_{i\gamma}$  represent the effects of the cation of type  $i$  on the refractive indices  $\alpha$ ,  $\beta$  and  $\gamma$ ,  $N_i$  is the number of the cations in a definite volume, the constant and one of the ion types, here Al(4), must be removed (equations 4–6), or the constant must be left out while Al(6) and Al(4) are combined (equations 7–9). It is possible to obtain solutions containing both constants and all ionic varieties but such equations cannot be ascribed any real importance (Hald, 1948).

*Refractive index of orthopyroxenes according to equations (1–3).*

*The constant and Al(4) are left out.*

Si, Al, Ti ... is the number of  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ti}^{4+}$  ions ... based on  $6\text{O}^{2-}$ .

$$\begin{aligned} \alpha = & (0.492 \pm 0.034)\text{Si} + (0.915 \pm 0.081)\text{Al}(6) + (1.634 \pm 0.258)\text{Ti} + \\ & (0.416 \pm 0.243)\text{Cr} + (0.576 \pm 0.083)\text{Fe}^{3+} + (0.387 \pm 0.033)\text{Fe}^{2+} + \\ & (0.407 \pm 0.047)\text{Mn} + (0.333 \pm 0.034)\text{Mg} + (0.422 \pm 0.073)\text{Ca} - \\ & (0.190 \pm 0.261)(\text{Na} + \text{K}). \end{aligned} \quad (4)$$

Table 1. Calculated and observed refractive indices of orthopyroxenes according to equations (4-6).

No. <sup>a</sup>	$\alpha_{\text{calc}}$	$\alpha_{\text{obs}}$	$\Delta_{\alpha}$	$\beta_{\text{calc}}$	$\beta_{\text{obs}}$	$\Delta_{\beta}$	$\gamma_{\text{calc}}$	$\gamma_{\text{obs}}$	$\Delta_{\gamma}$
1	1.651	1.651	0.000	1.654	1.653	-0.001	1.660	1.659	-0.001
2	1.661	1.660	-0.001	1.665	1.664	-0.001	1.669	1.669	0.000
3	1.668	1.668	0.000	1.674	1.673	-0.001	1.678	1.679	0.001
4	1.672	1.672	0.000	1.677	1.677	0.000	1.679	1.681	0.002
5	1.675	1.676	0.001	1.681	1.682	0.001	1.685	1.687	0.002
6	1.684	1.684	0.000	1.692	1.692	0.000	1.695	1.696	0.001
7	1.686	1.685	-0.001	1.694	1.693	-0.001	1.698	1.697	-0.001
8	1.694	1.691	-0.003	1.701	1.701	0.000	1.705	1.705	0.000
9	1.694	1.696	0.002	1.701	1.705	0.004	1.705	1.707	0.002
10	1.695	1.696	0.001	1.705	1.703	-0.002	1.706	1.708	0.002
11	1.694	1.693	-0.001	1.705	1.704	-0.001	1.709	1.709	0.000
12	1.702	1.702	0.000	1.712	1.712	0.000	1.716	1.715	-0.001
13	1.715	1.715	0.000	1.728	1.728	0.000	1.731	1.731	0.000
14	1.740	1.738	-0.002	1.751	1.749	-0.002	1.756	1.755	-0.001
15	1.752	1.751	-0.001	1.762	1.760	-0.002	1.769	1.769	0.000
16	1.754	1.755	0.001	1.763	1.763	0.000	1.770	1.773	0.003
17							1.668	1.670	0.002
18							1.673	1.675	0.002
19							1.680	1.680	0.000
20							1.677	1.680	0.003
21							1.682	1.683	0.001
22							1.688	1.689	0.001
23							1.690	1.692	0.002
24							1.698	1.698	0.000
25							1.698	1.699	0.001
26							1.705	1.707	0.002
27							1.717	1.721	0.004
28							1.725	1.726	0.001
29							1.727	1.730	0.003
30							1.731	1.731	0.000
31							1.733	1.735	0.002

<sup>a</sup> The numbers refer to Hori (1956), Tables 3 and 4.

$$\beta = (0.511 \pm 0.037)\text{Si} + (1.093 \pm 0.089)\text{Al}(6) + (1.921 \pm 0.284)\text{Ti} + (0.406 \pm 0.267)\text{Cr} + (0.508 \pm 0.092)\text{Fe}^{3+} + (0.381 \pm 0.036)\text{Fe}^{2+} + (0.358 \pm 0.051)\text{Mn} + (0.316 \pm 0.037)\text{Mg} + (0.263 \pm 0.081)\text{Ca} + (0.172 \pm 0.287)(\text{Na} + \text{K}). \quad (5)$$

$$\gamma = (0.531 \pm 0.012)\text{Si} + (0.971 \pm 0.021)\text{Al}(6) + (1.889 \pm 0.100)\text{Ti} + (0.711 \pm 0.066)\text{Cr} + (0.461 \pm 0.029)\text{Fe}^{3+} + (0.364 \pm 0.011)\text{Fe}^{2+} + (0.350 \pm 0.019)\text{Mn} + (0.299 \pm 0.012)\text{Mg} + (0.275 \pm 0.015)\text{Ca} + (0.068 \pm 0.033)(\text{Na} + \text{K}). \quad (6)$$

*Refractive index of orthopyroxenes according to equations (1-3).*

*The constant is left out while Al(6) and Al(4) are combined.*

Si, Al, Ti ... is the number of Si<sup>4+</sup>, Al<sup>3+</sup>, Ti<sup>4+</sup> ions ... based on 6O<sup>-2</sup>.

$$\alpha = (0.490 \pm 0.034)\text{Si} + (0.454 \pm 0.041)\text{Al} + (0.762 \pm 0.287)\text{Ti} + (0.010 \pm 0.271)\text{Cr} + (0.584 \pm 0.085)\text{Fe}^{3+} + (0.389 \pm 0.033)\text{Fe}^{2+} + (0.410 \pm 0.047)\text{Mn} + (0.335 \pm 0.034)\text{Mg} + (0.415 \pm 0.075)\text{Ca} - (0.166 \pm 0.266)(\text{Na} + \text{K}). \quad (7)$$



Table 2. Calculated and observed refractive indices of orthopyroxenes, observed and calculated values according to the equations (7-9).

No. <sup>a</sup>	$\alpha_{\text{calc}}$	$\alpha_{\text{obs}}$	$\Delta_{\alpha}$	$\beta_{\text{calc}}$	$\beta_{\text{obs}}$	$\Delta_{\beta}$	$\gamma_{\text{calc}}$	$\gamma_{\text{obs}}$	$\Delta_{\gamma}$
1	1.651	1.651	0.000	1.652	1.653	0.001	1.661	1.659	-0.002
2	1.661	1.660	-0.001	1.663	1.664	0.001	1.669	1.669	0.000
3	1.667	1.668	0.001	1.672	1.673	0.001	1.679	1.679	0.000
4	1.672	1.672	0.000	1.674	1.677	0.003	1.681	1.681	0.000
5	1.674	1.676	0.002	1.678	1.682	0.004	1.684	1.687	0.003
6	1.684	1.684	0.000	1.690	1.692	0.002	1.696	1.696	0.000
7	1.686	1.685	-0.001	1.693	1.693	0.001	1.697	1.697	0.000
8	1.694	1.691	-0.003	1.699	1.701	0.002	1.705	1.705	0.000
9	1.693	1.696	0.003	1.699	1.705	0.006	1.706	1.707	0.001
10	1.695	1.696	0.001	1.703	1.703	0.000	1.706	1.708	0.002
11	1.694	1.693	-0.001	1.702	1.704	0.002	1.709	1.709	0.000
12	1.701	1.702	0.001	1.710	1.712	0.002	1.715	1.715	0.000
13	1.715	1.715	0.000	1.726	1.728	0.002	1.732	1.731	-0.001
14	1.739	1.738	-0.001	1.748	1.749	0.001	1.756	1.755	-0.001
15	1.752	1.751	-0.001	1.760	1.760	0.000	1.770	1.769	-0.001
16	1.754	1.755	0.001	1.761	1.763	0.002	1.771	1.773	0.002
17							1.670	1.670	0.000
18							1.673	1.675	0.002
19							1.679	1.680	0.001
20							1.679	1.680	0.001
21							1.683	1.683	0.000
22							1.689	1.689	0.000
23							1.693	1.692	-0.001
24							1.698	1.698	0.000
25							1.699	1.699	0.000
26							1.705	1.707	0.002
27							1.719	1.721	0.002
28							1.726	1.726	0.000
29							1.730	1.730	0.000
30							1.731	1.731	0.000
31							1.736	1.735	-0.001

<sup>a</sup> The numbers refer to Hori (1956), Tables 3 and 4.

$$\begin{aligned} \beta = & (0.508 \pm 0.036)\text{Si} + (0.542 \pm 0.043)\text{Al} + (0.878 \pm 0.304)\text{Ti} - \\ & (0.084 \pm 0.287)\text{Cr} + (0.517 \pm 0.090)\text{Fe}^{3+} + (0.383 \pm 0.035)\text{Fe}^{2+} + \\ & (0.361 \pm 0.050)\text{Mn} + (0.318 \pm 0.036)\text{Mg} + (0.254 \pm 0.079)\text{Ca} + \\ & (0.203 \pm 0.282)(\text{Na} + \text{K}). \end{aligned} \quad (8)$$

$$\begin{aligned} \gamma = & (0.541 \pm 0.010)\text{Si} + (0.468 \pm 0.009)\text{Al} + (0.826 \pm 0.095)\text{Ti} + \\ & (0.371 \pm 0.059)\text{Cr} + (0.469 \pm 0.025)\text{Fe}^{3+} + (0.355 \pm 0.010)\text{Fe}^{2+} + \\ & (0.335 \pm 0.016)\text{Mn} + (0.289 \pm 0.010)\text{Mg} + (0.287 \pm 0.013)\text{Ca} + \\ & (0.123 \pm 0.028)(\text{Na} + \text{K}). \end{aligned} \quad (9)$$

Tables 1 and 2 show determined and calculated values for  $\alpha$ ,  $\beta$  and  $\gamma$ . It is apparent from these that the deviations are generally small. Table 3 illustrates changes in  $\gamma$  caused by the ionic substitution of 1 atom per cent of a ion with another for both ortho- and clinopyroxenes. A comparison between variations in the index of refraction of orthopyroxenes and clinopyroxenes, respectively, shows mostly a general agreement (increase or decrease of the index of refraction for corresponding substitution) but

Table 3. Changes in refractive index<sup>a</sup> of orthopyroxenes (Op) and clinopyroxenes (Cp) with ion substitutions by 1 per cent.

Substituting ion for Si, Ca, Mg or Fe <sup>2+</sup>									
	Al	Ti	Cr	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Mn	Mg	Ca <sup>2+</sup>	Na <sup>1+</sup>
Si	$\gamma \times 10^3$ (Op) $\gamma \times 10^3$ (Cp)	- 0.73 $\pm$ 0.13 - 1.14 $\pm$ 0.15							
Ca	$\gamma \times 10^3$ (Op) $\gamma \times 10^3$ (Cp)	+ 1.81 $\pm$ 0.16 + 0.95 $\pm$ 0.16	+ 0.84 $\pm$ 0.60 + 1.93 $\pm$ 0.60	+ 1.82 $\pm$ 0.28 + 2.22 $\pm$ 0.22	+ 0.68 $\pm$ 0.17 + 0.45 $\pm$ 0.17	+ 0.48 $\pm$ 0.21 - 0.16 $\pm$ 0.30	+ 0.02 $\pm$ 0.17 - 0.20 $\pm$ 0.16	— —	- 1.64 $\pm$ 0.31 - 1.40 $\pm$ 0.37
Mg	$\gamma \times 10^3$ (Op) $\gamma \times 10^3$ (Cp)	+ 1.79 $\pm$ 0.14 + 1.15 $\pm$ 0.15	+ 0.82 $\pm$ 0.60 + 2.13 $\pm$ 0.60	+ 1.80 $\pm$ 0.27 + 2.42 $\pm$ 0.21	+ 0.66 $\pm$ 0.14 + 0.65 $\pm$ 0.16	+ 0.46 $\pm$ 0.19 + 0.04 $\pm$ 0.29	— —	- 0.02 $\pm$ 0.17 + 0.20 $\pm$ 0.16	- 1.66 $\pm$ 0.30 - 1.20 $\pm$ 0.37
Fe <sup>2+</sup>	$\gamma \times 10^3$ (Op) $\gamma \times 10^3$ (Cp)	+ 1.13 $\pm$ 0.14 + 0.50 $\pm$ 0.16	+ 0.16 $\pm$ 0.60 + 1.48 $\pm$ 0.47	+ 1.14 $\pm$ 0.27 + 1.77 $\pm$ 0.22	— —	- 0.20 $\pm$ 0.19 - 0.61 $\pm$ 0.30	- 0.66 $\pm$ 0.14 - 0.65 $\pm$ 0.16	- 0.68 $\pm$ 0.17 - 0.45 $\pm$ 0.17	- 2.32 $\pm$ 0.30 - 1.85 $\pm$ 0.37

<sup>a</sup> The refractive indices  $\alpha$  and  $\beta$  are not included in the table owing to the large average error in the regression coefficients in the corresponding equations, depending on the limitations in the material studied (16 analyses).

Table 4. Ranges of the proportions of cations on the basis of six oxygen.

	$\alpha$ and $\beta$		$\gamma$	
	Min.	Max.	Min.	Max.
Si	1.875	2.004	1.875	2.004
Al (4)	0	0.093	0	0.104
Al (6)	0	0.073	0	0.073
Ti	0	0.013	0	0.017
Cr	0	0.020	0	0.020
Fe <sup>3+</sup>	0	0.061	0	0.061
Fe <sup>2+</sup>	0.011	1.592	0.011	1.592
Mn	0	0.222	0	0.222
Mg	0.223	1.970	0.223	1.970
Ca	0.012	0.076	0.005	0.162
Na + K	0	0.014	0	0.056

the numerical values may deviate widely.<sup>1</sup> This may partly be due to the fact that orthopyroxenes and clinopyroxenes do not have quite identical cell structures. Therefore the effect of the various ions on the index of refraction of the two mineral groups will not be exactly the same. It seems, however, that the main cause is attributable to other factors. It was found that when the range of variation for the ions making up the pyroxenes was great (see Table 4) good agreement was obtained between the two types of pyroxenes as well as between the corresponding values in the literature. When, for example, manganese is replaced by iron (divalent),  $\gamma$  for ortho- and clinopyroxenes is changed by respectively  $0.66 \times 10^{-3}$  and  $0.65 \times 10^{-3}$  per molecular per cent of substituent. The corresponding literature values are, respectively,  $0.63 \times 10^{-3}$  and  $0.68 \times 10^{-3}$  (Winchell, 1951), and  $0.59 \times 10^{-3}$  and  $0.60 \times 10^{-3}$  (Hess, 1949). Since the range of variation (for the ions making up the pyroxene) is small, incorrect determinations of a chemical and optical nature will strongly influence the exactness of the numerical values (see Tables 3 and 4). Therefore, with reference to this and the approximations that were necessary for mathematical reasons (Henriques, 1957) it was found that it is not possible to determine exactly the changes in the optical properties of pyroxenes caused by ionic substitution, with the material here used.

Hess and Phillips (1940) have found this for magnesian orthopyroxenes:

"The gamma index value seems to be practically independent of the  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{TiO}_2$  and alkalis contained in the mineral in small but variable amounts. Where lamellae of diopsidic pyroxene are present the CaO is probably contained almost exclusively in the lamellae, so it can have no effect on the optical properties of the orthopyroxene host. Where the lamellae are absent and one to three per cent of CaO is contained in the orthopyroxene, it still does not seem to make an appreciable change in the optical properties, and so may be neglected. ... Washington and Merwin<sup>2</sup> state that  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  should be considered as present in solid solution in the orthopyroxene and are not present in a separate molecule, such as the Tschermak molecule. The lack of effect of these trivalent oxides, as well as the other oxides mentioned above, with the possible exception of CaO, on the optical properties of

<sup>1</sup> A comparison between the regression coefficients in the corresponding equations of clinopyroxenes and orthopyroxenes as well as clinoamphiboles will be made in a later paper.

<sup>2</sup> Washington & Merwin: *Am. Jour. Sci.* 3, 119 (1922).

orthopyroxenes, suggests that these oxides present in small amounts may merely be included in holes in the crystal lattice and do not themselves form part of the lattice."

The investigation now performed, however, shows that the optical properties of the orthopyroxenes are dependent on all these ions (equations 4-9). Thus it is probable that the ions will form part of the pyroxene lattice.

The regression equations were solved with the aid of a digital computer (BESK), (Henriques, 1957).

#### REFERENCES

- HALD, A. (1948), *Statistiske metoder*. København.  
HENRIQUES, Å. (1957), The influence of cations on the optical properties of clinopyroxenes, Part I. *Arkiv för Mineralogi och Geologi* 2, 341-348.  
HESS, H. H. (1949), Chemical composition and optical properties of common clinopyroxenes, Part I. *Am. Min.* 34, 621-666.  
HESS, H. H., and PHILLIPS, A. H. (1940), Optical properties and chemical composition of magnesian orthopyroxenes. *Am. Min.* 25, 271-285.  
HORI, F. (1954), Effects of constituent cations on the optical properties of clinopyroxenes. *Scientific Papers of the College of General Education University of Tokyo*, IV, 71-83.  
—— (1956), Effects of constituent cations on the refractive indices of orthopyroxenes. *Mineralogical Journal*, Vol. 1, No. 6, 359-371 (Tokyo).  
WINCHELL, A. N., and WINCHELL, H. (1951), *Elements of Optical Mineralogy*, Part II, Fourth edition. New York.

Tryckt den 3 oktober 1958

Uppsala 1958. Almqvist & Wiksells Boktryckeri AB



## The influence of cations on the refractive index of clinoamphiboles

By ÅKE HENRIQUES

### SUMMARY

The optical properties  $\alpha$ ,  $\beta$ ,  $\gamma$  are correlated with chemical composition for clinoamphiboles by derivation of linear regression equations. Comparisons are made between clinopyroxenes and clinoamphiboles concerning the effect of the elements  $\text{Si}^{4+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^{+}$  on  $\alpha$ ,  $\beta$  and  $\gamma$ .

### Introduction

In a number of earlier papers the author has accounted for the optical properties of olivines as well as clino- and orthopyroxenes as a function of the chemical composition of the mineral (Henriques, 1957 and 1958*a*, *b*, *c*). A corresponding study has now been made on clinoamphiboles. The material investigated consists of about 40 amphiboles analysed and optically described in the literature (Table 1). The calculations were made using regression equations of the type:

$$\alpha = a_{\alpha} + a_{i\alpha}N_i, \quad (1)$$

$$\beta = a_{\beta} + a_{i\beta}N_i, \quad (2)$$

$$\gamma = a_{\gamma} + a_{i\gamma}N_i, \quad (3)$$

where  $a_{\alpha}$ ,  $a_{\beta}$  and  $a_{\gamma}$  are constants,  $a_{i\alpha}$ ,  $a_{i\beta}$  and  $a_{i\gamma}$  represent the effects of the cation of type  $i$  on the refractive indices  $\alpha$ ,  $\beta$  and  $\gamma$ .  $N$  is the number of the cations in a fixed volume.

All cations are included in the equations, even hydroxyl and fluoride ions. (Aluminium was, however, not divided into 4 and 6 coordinated.) The equations were also derived where consideration to hydroxyl and fluorine contents was not taken. These equations disclose, however, a lesser degree of agreement and were not included in this paper.

The regression equations were solved with a digital computer (BESK) by the method of least squares in accordance with the Gauss elimination method. The average error was calculated in accordance with the formula:

$$\left( X_{i, i+2} \cdot \frac{V^2}{m-n} \right)^{\frac{1}{2}}$$

where  $X_{i, i+2}$  is the diagonal element belonging to  $X_i$  in the diagonal element of the inverse matrix.

Table 1. Analyses  
Analyses 1-18: Van de Putte (1939); 1

	A									
	1	2	3	4	5	6	7	8	9	
SiO <sub>2</sub>	54.00	54.24	52.42	49.00	44.40	43.03	43.71	41.94	46.90	44
TiO <sub>2</sub>	0.16	0.27	0.71	0.10	1.50	2.55	0.34	3.40	—	0
Al <sub>2</sub> O <sub>3</sub>	0.20	—	1.30	3.90	11.22	10.69	10.71	7.26	7.16	12
Fe <sub>2</sub> O <sub>3</sub>	5.20	3.40	3.04	6.00	3.00	6.32	5.14	6.36	12.46	5
FeO	4.00	3.60	8.77	8.50	8.00	8.31	13.10	7.67	12.33	16
MnO	0.30	0.25	0.18	0.19	0.10	0.02	0.18	0.10	—	0
MgO	26.00	24.00	18.67	17.50	15.90	13.14	12.17	14.12	9.20	6
CaO	8.60	9.21	12.42	13.18	12.00	11.85	10.34	13.59	11.32	10
Na <sub>2</sub> O	0.43	1.24	1.20	1.10	1.55	2.75	1.30	3.67	—	1
K <sub>2</sub> O	0.19	0.47	—	0.08	0.86	—	0.54	—	—	0
H <sub>2</sub> O +	2.52	2.20	2.50	1.22	1.19	1.38	2.30	1.78	2.39	1
H <sub>2</sub> O -	—	—	—	—	—	—	—	—	—	—
F	1.42	0.59	0.42	—	—	—	—	—	—	—
Rem.	—	—	—	—	—	—	—	—	—	—
S	101.22	99.47	101.63	100.88	99.72	100.04	99.83	99.89	101.76	99
Less O for F	0.57	0.24	—	—	—	—	—	—	—	—
S	100.65	99.23	101.46	100.88	99.72	100.04	99.83	99.89	101.76	99
	21	22	23	24	25	26	27	28	29	30
SiO <sub>2</sub>	57.10	53.73	42.11	43.01	48.92	45.50	48.32	48.96	44.23	44
TiO <sub>2</sub>	0.35	0.41	2.76	2.87	1.21	1.73	1.43	1.07	1.81	3
Al <sub>2</sub> O <sub>3</sub>	6.19	2.72	10.05	12.01	5.88	9.66	6.43	7.85	14.62	10
Fe <sub>2</sub> O <sub>3</sub>	8.01	4.72	2.82	3.35	6.50	6.06	5.45	3.62	5.11	5
FeO	2.69	4.70	15.14	9.07	7.79	6.90	7.90	8.25	8.94	8
MnO	0.34	—	0.24	0.19	0.17	0.18	0.13	0.12	0.21	0
MgO	9.13	20.60	11.48	14.00	14.32	14.61	14.82	15.69	10.78	12
CaO	0.31	2.73	11.34	11.79	11.37	11.24	11.99	11.90	10.81	11
Na <sub>2</sub> O	9.77	7.42	1.01	1.08	1.20	1.20	0.99	1.04	1.51	1
K <sub>2</sub> O	2.38	1.82	1.43	1.01	0.71	0.92	0.67	0.53	0.61	2
H <sub>2</sub> O +	0.50	0.85	2.02	1.40	1.37	1.73	1.61	0.63	1.42	0
H <sub>2</sub> O -	—	—	0.06	0.06	0.18	0.19	0.06	0.08	0.08	0
F	2.69	0.92	—	0.84	0.27	tr.	tr.	1.41	0.22	0
Rem.	1.74 <sup>b</sup>	—	—	—	—	—	—	—	—	—
S	101.20	100.62	100.46	100.68	99.89	99.92	99.80	101.15	100.35	100
Less O for F	1.13	0.40	—	0.36	0.11	—	—	0.61	0.09	0
S	100.07	100.22	100.46	100.32	99.78	99.52	99.80	100.54	100.26	100

<sup>a</sup> Rem. is BaO 0.30, Cl 0.04.  
<sup>b</sup> Rem. is ZnO 0.59, Li<sub>2</sub>O 1.15.

the investigation.

ndius (1946); 23–31: Deer (1938); 32–39: Novotný (1949).

no.									
11	12	13	14	15	16	17	18	19	20
44.51	44.50	42.00	55.48	51.56	47.85	46.91	41.14	53.80	56.01
1.40	0.10	0.50	—	0.62	0.87	1.92	2.27	0.10	—
8.07	7.76	9.90	1.50	6.67	6.66	12.24	10.22	1.37	0.14
4.12	4.40	9.50	2.11	1.41	1.44	0.82	11.34	1.89	2.14
7.64	8.00	5.80	2.81	11.73	12.39	12.65	10.03	—	—
0.26	0.05	0.10	—	—	—	—	—	8.69	5.81
17.11	16.80	18.00	21.25	15.32	13.21	9.44	9.26	18.45	20.99
13.00	13.00	12.10	13.23	9.83	12.68	13.19	11.70	5.43	8.29
1.36	1.20	1.50	2.50	1.90	2.92	0.97	2.48	5.63	3.69
2.13	1.80	—	—	—	—	—	0.65	1.72	0.47
0.32	0.25	0.50	1.50	1.00	2.01	1.32	1.00	1.91	1.94
—	—	—	—	—	—	—	—	0.14	—
1.40	1.20	0.30	—	—	—	—	—	0.36	0.18
—	—	—	—	—	—	—	—	0.34 <sup>a</sup>	—
00.23	99.06	100.20	100.38	100.04	100.03	99.46	100.09	99.69	99.66
0.60	0.50	0.10	—	—	—	—	—	0.16	0.07
99.63	98.56	100.10	100.38	100.04	100.03	99.46	100.09	99.53	99.59
31	32	33	34	35	36	37	38	39	
47.14	56.16	52.91	52.54	46.38	39.37	42.28	41.27	41.26	
1.74	—	—	0.86	1.44	0.74	3.11	4.45	1.66	
9.44	1.28	7.91	4.69	13.50	15.22	12.83	13.62	11.10	
3.66	2.37	—	1.64	1.14	4.02	5.50	0.85	5.11	
8.38	3.92	6.85	6.43	5.79	20.81	7.77	13.02	18.70	
0.11	0.16	0.11	0.09	0.06	0.16	0.17	0.12	0.12	
14.44	21.37	16.51	17.12	16.20	4.30	11.87	11.10	5.23	
10.53	12.65	13.17	13.36	12.42	10.46	11.33	10.70	11.82	
1.15	0.37	0.26	0.88	1.34	1.54	1.19	1.31	1.66	
1.30	0.31	0.21	1.27	0.38	2.05	0.43	1.01	1.19	
2.00	—	—	—	—	—	—	—	—	
0.53	1.40	2.07	1.12	1.35	1.33	3.52	2.55	2.15	
—	—	—	—	—	—	—	—	—	
—	—	—	—	—	—	—	—	—	
100.42	99.93	100.00	100.00	100.00	100.00	100.00	100.00	100.00	
—	—	—	—	—	—	—	—	—	
100.42	99.99	100.00	100.00	100.00	100.00	100.00	100.00	100.00	

### The influence of cations on refractive index of clinoamphiboles

The regression equations here deduced for clinoamphiboles are:<sup>1</sup>

$$\alpha = (0.132 \pm 0.003)\text{Si} + (0.163 \pm 0.016)\text{Ti} + (0.109 \pm 0.003)\text{Al} + \\ (0.124 \pm 0.005)\text{Fe}^{3+} + (0.087 \pm 0.005)\text{Fe}^{2+} + (0.078 \pm 0.009)\text{Mn} + \\ (0.072 \pm 0.003)\text{Mg} + (0.060 \pm 0.006)\text{Ca} + (0.036 \pm 0.005)\text{Na} + \\ (0.030 \pm 0.016)\text{K} + (0.030 \pm 0.003)\text{OH}^- + (0.029 \pm 0.008)\text{F}. \quad (4)$$

$$\beta = (0.134 \pm 0.002)\text{Si} + (0.171 \pm 0.014)\text{Ti} + (0.111 \pm 0.003)\text{Al} + \\ (0.125 \pm 0.004)\text{Fe}^{3+} + (0.087 \pm 0.004)\text{Fe}^{2+} + (0.081 \pm 0.008)\text{Mn} + \\ (0.072 \pm 0.003)\text{Mg} + (0.058 \pm 0.005)\text{Ca} + (0.036 \pm 0.004)\text{Na} + \\ (0.015 \pm 0.014)\text{K} + (0.030 \pm 0.002)\text{OH}^- + (0.025 \pm 0.007)\text{F}. \quad (5)$$

$$\gamma = (0.133 \pm 0.002)\text{Si} + (0.158 \pm 0.015)\text{Ti} + (0.114 \pm 0.003)\text{Al} + \\ (0.123 \pm 0.005)\text{Fe}^{3+} + (0.083 \pm 0.005)\text{Fe}^{2+} + (0.075 \pm 0.009)\text{Mn} + \\ (0.071 \pm 0.003)\text{Mg} + (0.064 \pm 0.006)\text{Ca} + (0.038 \pm 0.005)\text{Na} + \\ (0.025 \pm 0.016)\text{K} + (0.035 \pm 0.003)\text{OH}^- + (0.026 \pm 0.008)\text{F}. \quad (6)$$

The corresponding equations for clinopyroxenes are:<sup>2</sup>

$$\alpha = (0.519 \pm 0.011)\text{Si} + (0.429 \pm 0.010)\text{Al} + (0.626 \pm 0.058)\text{Ti} + \\ (0.537 \pm 0.043)\text{Cr} + (0.542 \pm 0.018)\text{Fe}^{3+} + (0.370 \pm 0.012)\text{Fe}^{2+} + \\ (0.319 \pm 0.026)\text{Mn} + (0.305 \pm 0.011)\text{Mg} + (0.323 \pm 0.011)\text{Ca} + \\ (0.194 \pm 0.034)\text{Na} + (0.049 \pm 0.167)\text{K}. \quad (7)$$

$$\beta = (0.522 \pm 0.011)\text{Si} + (0.423 \pm 0.010)\text{Al} + (0.608 \pm 0.060)\text{Ti} + \\ (0.545 \pm 0.045)\text{Cr} + (0.558 \pm 0.018)\text{Fe}^{3+} + (0.367 \pm 0.012)\text{Fe}^{2+} + \\ (0.314 \pm 0.027)\text{Mn} + (0.301 \pm 0.011)\text{Mg} + (0.326 \pm 0.012)\text{Ca} + \\ (0.201 \pm 0.035)\text{Na} + (0.069 \pm 0.173)\text{K}. \quad (8)$$

$$\gamma = (0.533 \pm 0.011)\text{Si} + (0.419 \pm 0.10)\text{Al} + (0.682 \pm 0.059)\text{Ti} + \\ (0.517 \pm 0.045)\text{Cr} + (0.546 \pm 0.018)\text{Fe}^{3+} + (0.369 \pm 0.012)\text{Fe}^{2+} + \\ (0.308 \pm 0.027)\text{Mn} + (0.304 \pm 0.011)\text{Mg} + (0.324 \pm 0.012)\text{Ca} + \\ (0.184 \pm 0.035)\text{Na} + (0.168 \pm 0.172)\text{K}. \quad (9)$$

Observed and calculated values for  $\alpha$ ,  $\beta$  and  $\gamma$  in clinoamphiboles are given in Table 2. This indicates the deviations to be small. It should be observed that the derived equations are valid only for the now examined part of the clinoamphibole system (Table 3). This is especially obvious by a comparison between the optical properties calculated from the formulae and the real values of the pure end-members. In Table 4 the observed and calculated values for a number of amphibole end-members are included.

In Table 5 the dimension and the average error of the change in refractive indices  $\alpha$ ,  $\beta$  and  $\gamma$  in substitution have been calculated for the regression equations.

<sup>1</sup> Si, Ti, Al ... is the number of  $\text{Si}^{4+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Al}^{3+}$  ... ions based on  $24(\text{O}^{2-} + \text{OH}^- + \text{F}^-)$ .

<sup>2</sup> Si, Al, Ti ... is the number of  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Ti}^{4+}$  ... ions based on  $6\text{O}^{2-}$ .



Table 2. Refractive index of monoclinic amphiboles, observed and calculated values according to the equations (4)–(6).

	$\alpha_{\text{calc}}$	$\alpha_{\text{obs}}$	$\Delta\alpha$	$\beta_{\text{calc}}$	$\beta_{\text{obs}}$	$\Delta\beta$	$\gamma_{\text{calc}}$	$\gamma_{\text{obs}}$	$\Delta\gamma$
1	1.623	1.618	-0.005	1.633	1.626	-0.007	1.637	1.633	-0.004
2	1.619	1.620	0.001	1.629	1.628	-0.001	1.634	1.634	0.000
3	1.624	1.626	0.002	1.636	1.642	0.006	1.643	1.652	0.009
4	1.637	1.627	-0.010	1.649	1.646	-0.003	1.654	1.654	0.000
5	1.644	1.633	-0.011	1.657	1.652	-0.005	1.665	1.666	0.001
6	1.655	1.642	-0.013	1.671	1.662	-0.009	1.677	1.673	-0.004
7	1.652	1.655	0.003	1.665	1.667	0.002	1.676	1.676	0.000
8	1.651	1.659	0.008	1.665	1.669	0.004	1.673	1.677	0.004
9	1.656	1.655	-0.001	1.670	1.673	0.003	1.679	1.680	0.001
10	1.664	1.659	-0.005	1.677	1.673	-0.004	1.684	1.684	0.000
11	1.641	1.636	-0.005	1.646	1.643	-0.003	1.653	1.654	0.001
12	1.639	1.638	-0.001	1.644	1.644	0.000	1.651	1.654	0.003
13	1.657	1.675	0.018	1.670	1.684	0.014	1.674	1.692	0.018
14	1.611	1.610	-0.001	1.624	1.622	-0.002	1.631	1.631	0.000
15	1.640	1.632	-0.008	1.654	1.646	-0.008	1.653	1.655	0.002
16	1.636	1.643	0.007	1.650	1.657	0.007	1.659	1.666	0.007
17	1.643	1.650	0.007	1.659	1.665	0.006	1.667	1.675	0.008
18	1.670	1.663	-0.007	1.684	1.679	-0.005	1.689	1.685	-0.004
19	1.621	1.622	0.001	1.633	1.635	0.002	1.636	1.641	0.005
20	1.614	1.615	0.001	1.628	1.629	0.001	1.631	1.637	0.006
21	1.639	1.636	0.003	1.647	1.644	-0.003	1.651	1.649	-0.002
22	1.627	1.638	0.011	1.637	1.650	0.013	1.635	1.653	0.018
23	1.658	1.662	0.004	1.670	1.673	0.003	1.678	1.680	0.002
24	1.649	1.650	0.001	1.661	1.664	0.003	1.669	1.672	0.003
25	1.641	1.643	0.002	1.653	1.655	0.002	1.658	1.664	0.006
26	1.645	1.651	0.006	1.658	1.660	0.002	1.667	1.669	0.002
27	1.639	1.653	0.014	1.652	1.663	0.009	1.658	1.671	0.013
28	1.637	1.651	0.014	1.648	1.662	0.014	1.651	1.670	0.019
29	1.653	1.659	0.006	1.667	1.670	0.003	1.677	1.677	0.000
30	1.654	1.654	0.000	1.666	1.665	-0.001	1.670	1.673	0.003
31	1.641	1.651	0.010	1.653	1.661	0.008	1.663	1.669	0.006
32	1.614	1.612	-0.002	1.626	1.628	0.002	1.630	1.638	0.008
33	1.617	1.625	0.008	1.630	1.635	0.005	1.642	1.649	0.007
34	1.622	1.624	0.002	1.632	1.633	0.001	1.639	1.646	0.007
35	1.635	1.628	-0.007	1.650	1.643	-0.007	1.661	1.656	-0.006
36	1.675	1.675	0.000	1.685	1.683	-0.002	1.696	1.698	0.002
37	1.646	1.643	-0.003	1.661	1.661	0.000	1.678	1.699	0.021
38	1.656	1.655	-0.001	1.671	1.671	0.000	1.682	1.680	-0.002
39	1.665	1.672	0.007	1.676	1.680	0.004	1.688	1.696	0.008

A comparison between the average errors of the regression coefficients and between calculated and observed values for  $\alpha$ ,  $\beta$  and  $\gamma$  for clinoamphiboles and clinopyroxenes shows that the errors are of the same magnitude. With reference to the considerable variation in the contents of the material investigated and also the larger range of variation for amphiboles than pyroxenes, it would seem that the amphibole analyses have larger errors—both analytical and optical. (Inasmuch as exact details of the size of these errors is lacking no consideration was taken to their influence in deducing the equations.)

The range of variation is shown in Table 2 which shows boundary values for the cations in the unit cell, calculated on a basis of  $24(\text{O}^{2-} + \text{OH}^{-} + \text{F}^{-})$ .

Table 3. Ranges of the proportions of ions on the basis of  $24(\text{O}^{-2} + \text{OH}^{-} + \text{F}^{-})$ .

	Min.	Max.
Si	6.049	8.021
Al	0	2.802
Ti	0	0.491
Fe <sup>3+</sup>	0	1.366
Fe <sup>2+</sup>	0	2.717
Mn	0	1.060
Mg	1.000	5.247
Ca	0.046	2.176
Na	0	3.311
K	0	0.402
OH	0.253	3.358
F	0	1.195

A comparison between the regression coefficients in the clinoamphibole and clino-pyroxene equations is less illustrative, as the former are calculated on the basis of  $24(\text{O}^{-2} + \text{OH}^{-} + \text{F}^{-})$  ions while the latter are based on  $6\text{O}^{-2}$ . Therefore the relation number was calculated for the role of the various cations in the refractive indices (Table 6). The regression coefficient for cations was compared with that of silicon in both mineral groups, whose relation number was equated with 1. The table indicates (within the margin of error) that all ions, apart from  $\text{Ca}^{2+}$  and  $\text{Na}^{+1}$ , show about the same effect on the refractive index in both mineral groups. This is probably due to the similar atomic structure of the amphiboles and the pyroxenes and the close agreement in the bonding distance and also to the fact that Ca and Na in the amphiboles partially occur in other positions in the lattice.

In the above connexion orthopyroxenes display similarity with clinoamphiboles with respect to  $\gamma$ . For  $\alpha$  and  $\beta$  the average errors are large.

Table 4. Refractive index of end-members, calculated<sup>a</sup> and observed<sup>b</sup> values.

		$\alpha$		$\beta$		$\gamma$	
		calc	obs	calc	obs	calc	obs
Grunerite	$\text{H}_2\text{Fe}_7\text{Si}_8\text{O}_{24}$	1.725	1.685	1.741	1.709	1.715	1.728
Tremolite	$\text{H}_2\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{24}$	1.596	1.600	1.608	1.613	1.617	1.624
Ferrotremolite	$\text{H}_2\text{Ca}_2\text{Fe}_5\text{Si}_8\text{O}_{24}$	1.671	1.688	1.683	1.699	1.677	1.704
Arfvedsonite	$\text{H}_2\text{Na}_3\text{Fe}_4^{2+}\text{Fe}_3^{3+}\text{Si}_8\text{O}_{24}$	1.696	1.693	1.713	1.696	1.703	1.698
Riebeckite	$\text{H}_2\text{Na}_2\text{Fe}_3^{2+}\text{Fe}_2^{3+}\text{Si}_8\text{O}_{24}$	1.697	1.685	1.715	1.687	1.705	1.689
			-1.695		-1.697		-1.699
Glaucophane	$\text{H}_2\text{Na}_2\text{Mg}_3\text{Al}_2\text{Si}_8\text{O}_{24}$	1.622	1.606	1.642	1.622	1.651	1.627

<sup>a</sup> According to equations (4-6).

<sup>b</sup> According to Tröger (1952).

<sup>1</sup> On account of the low contents of  $\text{K}^{+}$  and its slight range of variation, its relation numbers were not calculated.

Table 5. Changes in the refractive indices of monoclinic amphiboles with ion substitution by 1 per cent.

	Substituting ion						
	Al	Ti	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Mn	Mg	Na
Si							
$\delta\alpha \times 10^3$	-0.23 ± 0.04			+0.27 ± 0.08	+0.18 ± 0.11	+0.12 ± 0.07	-0.24 ± 0.08
$\delta\beta \times 10^3$	-0.23 ± 0.04		+0.64 ± 0.08	+0.29 ± 0.06	+0.23 ± 0.09	+0.14 ± 0.06	-0.22 ± 0.06
$\delta\gamma \times 10^3$	-0.19 ± 0.04		+0.67 ± 0.06	+0.19 ± 0.08	+0.11 ± 0.11	+0.07 ± 0.07	-0.26 ± 0.08
Ca							
$\delta\alpha \times 10^3$	+0.49 ± 0.07	+1.03 ± 0.17					
$\delta\beta \times 10^3$	+0.53 ± 0.06	+1.13 ± 0.15					
$\delta\gamma \times 10^3$	+0.50 ± 0.07	+0.94 ± 0.16					
Mg							
$\delta\alpha \times 10^3$	+0.37 ± 0.04	+0.91 ± 0.16	+0.52 ± 0.06	+0.15 ± 0.06	+0.06 ± 0.10	—	-0.12 ± 0.07
$\delta\beta \times 10^3$	+0.39 ± 0.04	+0.99 ± 0.14	+0.53 ± 0.05	+0.15 ± 0.05	+0.09 ± 0.09	—	-0.14 ± 0.06
$\delta\gamma \times 10^3$	+0.43 ± 0.04	+0.87 ± 0.15	+0.52 ± 0.06	+0.12 ± 0.06	+0.04 ± 0.10	—	-0.07 ± 0.07
Fe <sup>2+</sup>							
$\delta\alpha \times 10^3$	+0.22 ± 0.06	+0.76 ± 0.17	+0.37 ± 0.07	—	-0.09 ± 0.10	-0.15 ± 0.06	-0.27 ± 0.08
$\delta\beta \times 10^3$	+0.24 ± 0.05	+0.84 ± 0.15	+0.38 ± 0.06	—	-0.06 ± 0.09	-0.15 ± 0.05	-0.29 ± 0.06
$\delta\gamma \times 10^3$	+0.31 ± 0.06	+0.75 ± 0.16	+0.40 ± 0.07	—	-0.08 ± 0.10	-0.12 ± 0.06	-0.19 ± 0.08

Table 6.

	Clinoamphiboles			Clinopyroxenes			Orthopyroxenes		
	$\alpha$	$\beta$	$\gamma$	$\alpha$	$\beta$	$\gamma$	$\alpha$	$\beta$	$\gamma$
Si	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Al	1.21 ± 0.04	1.21 ± 0.04	1.17 ± 0.04	1.21 ± 0.04	1.23 ± 0.04	1.27 ± 0.04	1.08 ± 0.12	0.94 ± 0.10	1.15 ± 0.03
Ti	0.81 ± 0.08	0.78 ± 0.07	0.84 ± 0.08	0.83 ± 0.08	0.86 ± 0.09	0.78 ± 0.07	0.64 ± 0.24	0.58 ± 0.22	0.65 ± 0.08
Fe <sup>3+</sup>	1.06 ± 0.05	1.07 ± 0.04	1.08 ± 0.05	0.96 ± 0.04	0.94 ± 0.04	0.98 ± 0.04	0.84 ± 0.14	0.98 ± 0.19	1.15 ± 0.07
Fe <sup>2+</sup>	1.52 ± 0.10	1.54 ± 0.08	1.60 ± 0.10	1.40 ± 0.06	1.42 ± 0.06	1.44 ± 0.06	1.26 ± 0.14	1.33 ± 0.15	1.52 ± 0.05
Mn	1.69 ± 0.20	1.65 ± 0.17	1.77 ± 0.22	1.63 ± 0.14	1.66 ± 0.15	1.73 ± 0.16	1.19 ± 0.16	1.41 ± 0.22	1.61 ± 0.08
Mg	1.83 ± 0.09	1.86 ± 0.09	1.87 ± 0.09	1.70 ± 0.07	1.73 ± 0.07	1.75 ± 0.07	1.46 ± 0.15	1.60 ± 0.21	1.87 ± 0.07
Ca	2.20 ± 0.22	2.31 ± 0.20	2.08 ± 0.20	1.61 ± 0.07	1.60 ± 0.07	1.63 ± 0.07	1.18 ± 0.23	2.00 ± 0.62	1.88 ± 0.09
Na	67 ± 0.51	3.72 ± 0.42	3.50 ± 0.47	2.68 ± 0.47	2.60 ± 0.46	2.90 ± 0.55	—	—	—

This is probably partly due to the strongly limited nature of the material studied (16 analyses for  $\alpha$  and  $\beta$ ) whereby variations in the contents and range of variation are small for the composite ions, and partly due to relatively large errors in the analyses.

#### ACKNOWLEDGEMENTS

The author wishes to convey his thanks to Dr. K. Arle and Mr. L. Jansson for mathematical collaboration.

#### REFERENCES

- DEER, W. A. (1938), The composition and paragenesis of the hornblendes of the Glen Tilt complex, Perthshire. *Min. Mag.* 25, 56-74.
- HENRIQUES, Å. (1957), The effect of cations on the optical properties and the cell-dimensions of knebelite and olivine. *Arkiv för Mineralogi och Geologi* 2, No. 17, 305-313.
- (1958a), An attempt to determine the effect of cations on the extinction angle of clinopyroxene  $c \wedge \gamma$  with the aid of linear regression equations. *Arkiv för Mineralogi och Geologi* 2, No. 21, 337-340.
- (1958b), The influence of cations on the optical properties of clinopyroxenes. Part. I, *Arkiv för Mineralogi och Geologi* 2, No. 22, 341-348.
- (1958c), The influence of cations on the optical properties of clinopyroxenes. Part. II, *Arkiv för Mineralogi och Geologi* 2, No. 29, 385-390.
- NOVOTNÝ, M. (1949), On the chemical composition and physical properties of some Moravian amphiboles. *Acta Acad. Sci. Nat. Moravo-Silesiaca*, Brno. 21, No. 10.
- PUTTE, R. VAN DE (1939), Contribution à l'étude des amphiboles. *Mus. Belgique, Bull.* 15, no 31.
- SUNDIUS, N. (1946), The classification of the hornblendes and the solid solution relations in the amphibole group. *Sveriges Geol. Undersökning, Ser. C*, no. 480.
- TRÖGER, W. E. (1952), Tabellen zur optischen Bestimmung der gesteinsbildenden Minerale.

Tryckt den 3 oktober 1958

Uppsala 1958. Almqvist & Wiksells Boktryckeri AB









## INNEHÅLL

	Sid.
16. GABRIELSON, O., The crystal structure of mendipite, $Pb_3O_2Cl_2$ . . . . .	299-304
17. HENRIQUES, Å., The effect of cations on the optical properties and the cell-dimensions of knebelite and olivine . . . . .	305-313
18. BLIX, R., GABRIELSON, O. and WICKMAN, F. E., Jagoite, a new lead-silicate mineral from Långban in Sweden . . . . .	315-317
19. SUNDIUS, N., Alkaline rocks and carbonates of alkalies, calcium and magnesium . . . . .	319-331
20. BOSTRÖM, K., The chemical composition and symmetry of caryinite . .	333-336
21. HENRIQUES, Å., An attempt to determine the effect of cations on the extinction angle of clinopyroxene $c \wedge \gamma$ with the aid of linear regression equations . . . . .	337-340
22. HENRIQUES, Å., The influence of cations on the optical properties of clinopyroxenes. Part I . . . . .	341-348
23. HENRIQUES, Å., On the determination of the composition of garnet without chemical analyses . . . . .	349-352
24. ODHNER, N. H., Fundamental argument in cenozoic geology dynamic factors: Crustal undulations, thermal dilatation and constriction . .	353-367
25. HENRIQUES, Å., Amphitalite a mixture . . . . .	369
26. HENRIQUES, Å., Tetragophosphite discredited . . . . .	371-372
27. WELIN, E., Notes on the mineralogy of Sweden. 1-2 . . . . .	373-379
28. HENRIQUES, Å., The influence of cations on the optical properties of clinopyroxenes. Part II . . . . .	381-384
29. HENRIQUES, Å., The influence of cations on the optical properties of orthopyroxenes . . . . .	385-390
30. HENRIQUES, Å., The influence of cations on the refractive index of clinoamphiboles . . . . .	391-398

---

Arkiv för Mineralogi och Geologi utgives i tvångsfritt utkommande häften. Sex dylika bilda ett band. — Pris för detta häfte Kr. 9:—.

Arkiv för Mineralogi och Geologi appears at irregular intervals. Six numbers will form one volume. — The price of this number Sw. Crs. 9:—.

---

*Utgivet den 20 november 1958.*